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(54) **Process for the preparation of containment barriers impermeable to fluids**

(57) Process for the preparation of containment barriers impermeable to fluids, which comprises:

a) hydraulic fracturing of the ground to create extensive fissures, the above fracturing being effected by injecting, under pressure and through wells, compositions selected from:

- i) aqueous solutions or dispersions of materials capable of gelling;
- ii) aqueous dispersions of solids;
- iii) materials, or relative solutions/dispersions, capable of solidifying on cooling;

b) subsequent maintenance under pressure until the formation of the above containment barriers, essentially consisting of compositions (i)-(iii).

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Description

[0001] The present invention relates to a process for the preparation of containment barriers impermeable to fluids. The above barriers can be used for blocking the movement of pollutants in the ground and removing pollutants from groundwater.

[0002] The term "Pump-and-treat" is a general term used for any technique capable of removing polluted groundwater and treating it outside the polluted area, usually on the surface.

[0003] Treatment methods can vary, but basically the water is pumped out of the polluted area underground; purification is then effected on the surface. The "Pump-and-treat" technique is typically used for contaminants dissolved in groundwater. However also the removal of non-aqueous liquid phases (NAPLs), both light and heavy, can be carried out with special pumping methods.

[0004] "Pump-and-treat" systems can be designed, installed and put into operation according to techniques well known to experts in the field.

[0005] Under favourable geological conditions, the pumping systems allow a rapid removal of polluted masses from areas where contaminants are present in greater quantities. For this reason the "pump-and-treat" technique continues to be the most widely used method for limiting and controlling polluted areas.

[0006] The time necessary for drainage however can be excessively lengthy and in many cases the objective is not reached. For example, in the presence of NAPLs, the concentration of contaminants in the groundwater can return to levels practically the same as originally after a short interruption in the pumping. This occurs because the large residual masses of pollutants slowly dissolve in the groundwater. Alternative technologies are being studied to solve this problem, for draining sites in shorter times and at lower costs.

[0007] One of the most promising techniques comprises injection into groundwater of co-solvents and mixtures of surface-active agents, particularly those which form micro-emulsions. This technique has recently been used on site with excellent results.

[0008] In fact, the micro-emulsion technique allows a more effective removal of pollutants, increasing their apparent solubility in water. In addition this technique favours the mobility of NAPLs reducing the interfacial tension between water and contaminant. The micro-emulsions are then injected into the area in question from injection wells and then recovered on the surface (where they are processed) together with the water and contaminants coming from other wells; in this way the aquifer swept clean. Volumes of water are then injected to remove residues of the surface-active agents.

[0009] A critical problem for treatment using surface-active agents lies in the uncontrolled migration of the contaminants during draining operations. Owing to the enormously increased solubility and mobility of NAPLs

and other contaminants adsorbed into the earth matrix, the possibility of lateral or vertical migration of the contaminated area is a source of potential risk. To solve this problem, efforts are moving towards the use of containment barriers. This technique (i.e. the use of containment barriers) is becoming more and more widely used as a component of all "pump-and-treat" techniques, as the barriers isolate the areas to be treated with a consequent reduction in the total volume to be treated and a saving in cost and time.

[0010] Containment barriers are at present constructed using traditional materials and techniques, for example sheet piles and trenches filled with cement or impermeable mixtures of clay and earth. The present technology of containment barriers however has several serious limitations. For example barriers which do not penetrate to a sufficient depth are not very effective. On the contrary, it is becoming increasingly more necessary to adopt technologies, which are not available at the moment, for constructing deep containment barriers.

[0011] It is still extremely difficult, moreover, to construct horizontal barriers, i.e. below polluted areas, capable of blocking the movement of pollutants towards greater depths.

[0012] A process has now been found for the preparation of containment barriers which overcomes the disadvantages described above.

[0013] In accordance with this, the present invention relates to a process for the preparation of containment barriers impermeable to fluids, which comprises:

a) hydraulic fracturing of the ground to create extensive fissures, the above fracturing being effected by injecting, under pressure and through wells, compositions selected from:

- (i) aqueous solutions or dispersions of materials capable of gelling;
- (ii) aqueous dispersions of solids;
- (iii) materials, or relative solutions/dispersions, capable of solidifying on cooling;

b) subsequent maintenance under pressure until the formation of the above containment barriers essentially consisting of compositions (i) - (iii).

[0014] In the case of gelable materials (i), the containment barriers are formed by the gelation of gelable substances contained in (i).

[0015] In the case of aqueous dispersions of solids (ii), the barriers are formed as a result of the creation of impermeable filter cakes.

[0016] In the case of materials (iii), or relative solutions/dispersions, capable of solidifying on cooling, the barriers are obviously formed following a lowering in the temperature.

[0017] The term gelable aqueous solution (or dispersion) refers to the essentially aqueous solution (or dis-

persion) of substances which from an initial viscosity ranging from 1 to 200 mPas are transformed into viscoelastic solids (gel) having elastic modulus values higher than 1 Pa, preferably greater than 10 Pa.

[0018] Aqueous solutions or dispersions (i) of materials capable of gelling can be divided into three categories, a first category (ia) essentially consisting of polymers in the presence of, or without, cross-linking agents. In this case gelation takes place by means of the cross-linking of the polymers present in the solution/dispersion. This category comprises guar in the presence of cross-linking agents selected from polyvalent metal ions (for example B^{+3} , Zr^{+4} , Ti^{+4} , Sb^{+}) which give rise to cross-linking within pH ranges characteristic for each single metal ion (for example at pH 8-12 for B^{+3} , at pH 7-10 for Zr^{+4} , at pH 7-9 for Ti^{+4} , at pH 3-6 for Sb^{+}), HPG (hydroxypropyl guar) cross-linkable in the presence of the same metal ions and within the same pH ranges specified above, CMHPG (carboxymethylhydroxypropyl guar) also cross-linkable in the presence of polyvalent metal ions (for example Zr^{+4} at pH from 3 to 6, Ti^{+4} at pH from 7 to 9, Al^{+3} at pH from 4 to 6), (co)polyacrylamides also cross-linkable with polyvalent ions, for example Al^{+3} and Zr^{+4} at pH from 4 to 6, "Xanthan Gum" cross-linkable with Ti^{+4} and B^{+3} , ligninsulfonates, cellulose derivatives such as carboxymethylcellulose (known as CMC) and derivativized hydroxyethylcellulose (known as DDMEC) cross-linkable with polyvalent metal ions, amides functionalized with phosphoric esters, polysaccharides functionalized with anionic groups, so-called physical gels (a typical example is polypropylene glycol, fluid when hot and gel at temperatures lower than about 30°C).

[0019] A second category (ib) consists of aqueous solutions (or dispersions) of monomers capable of polymerizing and then cross-linking. Typical but non-limiting examples are monomers belonging to the group of acrylamides which are cross-linkable in the presence of suitable agents, such as radical initiators.

[0020] A third category (ic) consists of solutions and/or dispersions of sodium and/or potassium silicates, which gel within suitable pH ranges.

[0021] As far as aqueous dispersions of solids (ii) are concerned, typical examples are dispersions of clays, calcium carbonates, colloidal polymers (for example CMC, i.e. carboxymethylcellulose and its derivatives), lignite, cross-linked modified amides and relative mixtures. The above dispersions (ii) do not gel but, owing to filtration of the solution into the ground surrounding the fracture, produce impermeable filter cakes.

[0022] Typical examples of materials (iii), or relative solutions/dispersions, capable of solidifying on cooling are waxes (for example "Montan wax").

[0023] The solutions or dispersions (i)-(iii) may also contain other additives usually used in gelable aqueous formulations. Typical examples are biocides, gelation retarding agents, buffer and pH control substances, viscosity regulators (for example "xanthan gum").

[0024] Other substances contained in these solutions/dispersions are fluid-loss control additives, such as calcium carbonate, bentonite, polymers (for example lignite), modified amides, solids having dimensions $> 5 \mu m$, as well as substances added for the purpose of keeping the fracture produced by the gel/gelling agent (known as "proppant" substances) open.

[0025] The gels (or filter cakes) formed from the solutions/dispersions (i) have permeability values of the order of microdarcy and which are therefore such as to prevent flow through or across the fracture. In addition, the gels may or may not be biodegradable, depending on the material used. This is a great advantage when, at the end of the draining operation, the previous situation must be re-established.

[0026] In the case of the dispersions (ii), these materials allow the formation of filter cakes capable of preventing the fluid from spreading across the barrier into the surrounding areas.

[0027] With respect to the hydraulic fracturing technique, this is widely used in the petroleum industry for stimulating the productivity of oil wells (see for example "Basic Principles of Hydraulic Fracturing"). In short, the hydraulic fracturing technique consists in injecting liquids (usually water) at high pressure into the drilling well until the pressure exceeds critical values and produces fractures (or widens pre-existing fractures). The fracturing technique has also recently been used in the field of ground drainage. In fact, fracturing helps to introduce materials used for other innovative ground drainage technologies (for example the introduction of substances capable of improving biological remediation, the introduction of conductive substances for improving electrokinetic processes, the introduction of reagent materials such as zero-valent iron or permanganate).

[0028] The prior art on the other hand does not disclose the use of the fracturing technique for introducing gelable substances or substances suitable for forming impermeable filter cakes.

[0029] As far as the time necessary for cross-linking/gelling the solutions/dispersions (i) is concerned, i.e. the duration of step (b), this can be regulated by experts in the field according to known procedures. For example the gelation can be varied in relation to the concentration and type of metal ion, the pH, the type and concentration of the peroxide.

[0030] In any case, it is always preferable to use times which are much higher than the minimum times necessary for gelation/cross-linking or for the formation of filter cakes.

[0031] The use of gelling solutions/dispersions for isolating NAPLs has already been proposed (see I. Lakatos, 1997 International Containment Technology Conference and Exhibition, St. Petersburg, Florida, USA). The above proposals however are based on the method of placing the gelling agent by infiltration from a series of wells. This technique is expensive as it requires large volumes of gel as the gel expands radially

from the well; in addition this technique does not ensure the formation of adequate barriers.

[0032] The injection of the solutions/dispersions of the present invention is much simpler and less expensive as it requires a lower number of wells and treatment times. In addition, the presence of gelled barriers or impermeable filter cakes, as well as reducing the total number of sampling wells, also eliminates the risk of the pollution migrating beyond the sampling wells. This is particularly important in drainage processes carried out in the presence of micro-emulsions.

[0033] Another advantage of the process of the present invention lies in the fact that, when considered appropriate, it is possible to prepare biodegradable containment barriers. As a result, after drainage operations, the above barriers can be eliminated by means of biological degradation.

[0034] In addition the process of the present invention allows the preparation of barriers also at great depths, which is not possible with traditional techniques.

[0035] Finally, an important element lies in the fact that the barriers/filter cakes of the present invention can be either vertical or horizontal.

Claims

1. A process for the preparation of containment barriers impermeable to fluids, which comprises:
 - a) hydraulic fracturing of the ground to create extensive fissures, the above fracturing being effected by injecting, under pressure and through wells, compositions selected from:
 - (i) aqueous solutions or dispersions of materials capable of gelling;
 - (ii) aqueous dispersions of solids;
 - (iii) materials, or relative solutions/dispersions, capable of solidifying on cooling;
 - b) subsequent maintenance under pressure until the formation of the above containment barriers essentially consisting of compositions (i) - (iii).
2. The process according to claim 1, characterized in that the aqueous solutions or dispersions of materials capable of gelling (i) are selected from:
 - (ia) aqueous solutions and/or dispersions essentially consisting of polymers in the presence of or without cross-linking agents;
 - (ib) aqueous solutions of monomers capable of polymerizing and then cross-linking;
 - (ic) solutions and/or dispersions of sodium and/or potassium silicates, which gel within suitable pH ranges.
3. The process according to claim 2, wherein the compositions (ia) are selected from solutions/dispersions of:
 - 3a) guar, hydroxypropyl guar, carboxymethyl-hydroxypropyl guar, in the presence of polyvalent metal ions;
 - 3b) (co)polyacrylamides in the presence polyvalent metal ions;
 - 3c) xanthan gum in the presence of Ti^{+4} or B^{3+} ions;
 - 3d) ligninsulfonates;
 - 3e) cellulose derivatives, amides modified with phosphoric esters, polysaccharides functionalized with anionic groups, in the presence of polyvalent metal ions;
 - 3f) physical gels.
4. The process according to claim 2, characterized in that the compositions (ib) essentially consist of solutions (or dispersions) of monomers belonging to the group of acrylamides, cross-linkable in the presence of suitable cross-linking agents.
5. The process according to claim 4, characterized in that the cross-linking agents are radical initiators.
6. The process according to claim 1, characterized in that the dispersions (ii) are selected from dispersions of clays, calcium carbonates, colloidal polymers, lignite, modified amides and relative mixtures.
7. The process according to claim 1, characterized in that the materials (iii) are waxes.



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EUROPEAN SEARCH REPORT

Application Number
EP 99 11 8831

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 5 503 227 A (SAPONJA JEFFREY C ET AL) 2 April 1996 (1996-04-02) * column 5, line 17 - line 32 *	1	E21B33/138 E02D19/16
Y	* column 5, line 40 - line 45; claims 16,17 *	2-7	
X	US 5 002 431 A (HEYMANS MICHAEL J ET AL) 26 March 1991 (1991-03-26) * column 2, line 19 - line 33 *	1	
Y	* column 3, line 58 - column 5, line 2; figure 1 *	2-4	
X	US 3 688 507 A (MULLER DONALD SINCLAIR) 5 September 1972 (1972-09-05) * column 1, line 28 - line 40 *	1	
	* column 2, line 7 - line 13 *		
	* column 4, line 20 - line 29 *		
Y	US 3 669 189 A (FISCHER PAUL W) 13 June 1972 (1972-06-13) * column 4, line 14 - line 24 *	5	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
Y	US 4 279 547 A (CLEM ARTHUR G) 21 July 1981 (1981-07-21) * column 2, line 52 - column 3, line 17 *	6,7	E21B E02D
A	US 4 790 688 A (CASTOR TREVOR P) 13 December 1988 (1988-12-13) * column 2, line 20 - line 37 *	1-4	
	* column 3, line 19 - line 30 *		
	* column 3, line 57 - line 66 *		
	* column 4, line 31 - column 5, line 17 *		
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 13 January 2000	Examiner Bellingacci, F
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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13-01-2000

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5503227	A	02-04-1996	NONE		
US 5002431	A	26-03-1991	NONE		
US 3688507	A	05-09-1972	DE	2011823 A	08-10-1970
			GB	1257569 A	22-12-1971
			ZA	7001717 A	28-04-1971
US 3669189	A	13-06-1972	CA	967903 A	20-05-1975
US 4279547	A	21-07-1981	US	4209568 A	24-06-1980
			AU	5026879 A	27-03-1980
			BE	878352 A	17-12-1979
			DE	2936580 A	27-03-1980
			FR	2436172 A	11-04-1980
			GB	2030155 A	02-04-1980
			IT	1120008 B	19-03-1986
			JP	55042291 A	25-03-1980
			NL	7905880 A	20-03-1980
			SE	7907663 A	19-03-1980
US 4790688	A	13-12-1988	NONE		