



(22) Date de dépôt/Filing Date: 1994/04/20

(41) Mise à la disp. pub./Open to Public Insp.: 1994/10/22

(45) Date de délivrance/Issue Date: 2006/06/13

(30) Priorité/Priority: 1993/04/21 (FR93 04802)

(51) Cl.Int./Int.Cl. *C04B 14/00* (2006.01),
E21B 33/14 (2006.01), *C04B 20/00* (2006.01),
C09K 8/46 (2006.01)

(72) Inventeurs/Inventors:
MAROY, PIERRE, FR;
BARET, JEAN-FRANCOIS, FR

(73) Propriétaire/Owner:
SCHLUMBERGER CANADA LIMITED, CA

(74) Agent: SMART & BIGGAR

(54) Titre : LAITS DE CIMENT POUR Puits DE PETROLE, METHODE DE PREPARATION ET UTILISATION POUR LA CIMENTATION

(54) Title: OILWELLS CEMENT SLURRIES, THEIR PREPARATION AND THEIR USE IN WELL CEMENTING OPERATION

(57) **Abrégé/Abstract:**

The particulate phase of cement slurries according to the present invention comprises particles which have specifically adapted size ranges or granulometries. All the essential properties of slurry and its cost are very clearly improved. Application to all the well cementing operations in oil wells or the like.

55-162/STL

PATENT APPLICATION

OILWELLS CEMENT SLURRIES
THEIR PREPARATION AND THEIR USE IN WELL CEMENTING OPERATION

Invention: Pierre MAROY
Jean François BARET

Applicant: DOWELL SCHLUMBERGER
(Compagnie des Services, S.A)

ABSTRACT OF THE INVENTION

The particulate phase of cement slurries according to the present invention comprises particles which have specifically adapted size ranges or granulometries.

All the essential properties of slurry and its cost are very clearly improved.

Application to all the well cementing operations in oil wells or the like.

OILWELLS CEMENT SLURRIES
THEIR PREPARATION AND THEIR USE IN WELL CEMENTING OPERATION.

5

The present invention relates to the technical domain of annulus cementing of oil, water and geothermal wells or the like.

10

These operations have been very well known in the art, as well as in their principle that in their performance ; the great difficulties of their performance have been also well known.

Thus, these data would be really uselessly recalled here. That is why only the essential will be briefly mentioned below.

15

The well cementing operation consists schematically of preparing at the surface a cement slurry which is then pumped under pressure into the tubing or casing. Such downwardly pumped slurry displaces the drilling mud which circulates up the surface (where it is carried off) through the annulus, i.e. the area between the borehole and the casing.

20

The cement slurry is itself displaced by an inert fluid, the pumped volumes computations being so as the pumping is stopped when the mud has been replaced by the slurry in the annulus, while a inert fluid is into the inside of the casing. The cement slurry is then let to set into the annulus. This set cement has then two functions : isolation of the different underground zones and casing mechanical support.

25

It has been appreciated that, to succeed in carrying out such an operation, the mastering or monitoring of the slurry rheology is of primary importance.

30

The control of very numerous parameters is also of prime concern : fluid loss, free water, settling, thickening time (or "TT"), development of compressive strength, especially at the beginning of the settling, etc..., cement permeability testing against the fluids which degrade it, etc....

35

It must also be appreciated that, since the temperature and pressure cycles to which the cement slurry is submitted, i.e. surface → downhole → surface, are entirely specific of the considered industry, the preceeding subjects are extremely difficult to solve.

Further more, the adjustment of the cement slurry density is also very important for ensuring the hydrostatic equilibrium. If the density is too low, the risk is that external fluids may migrate towards the casing and may be then the cause of damages. If, on the contrary, the density is too high, the risk is that
5 fracturing fragile formation may occur with serious consequences. These risks and their inherent requirements are also very specific of the considered industry. All this is also very well known in the art.

10 Numerous additives of different kinds are also known and they are used in the art alone or in various combinations in order to design the better possible slurry for a given well.

This slurry design is never easy. This is often imperfect because many required properties imply using antagonistic means.

15 On the other hand, a certain degree of uncertainty is always present as far as the bottom hole conditions, for example, maximal temperature, thief zones presence etc..., are concerned. In the prior art, these uncertainties imply, for example, an overdose of some additive(s) to avoid a major risk.

This implies an important complexity of slurry design, used means and
20 used additives, with the inherent risks and costs.

The present invention provides a design technique of the cement slurries, characterized by a great simplicity, a low cost, and the excellence of the achieved properties. A spectacular improvement of all the useful
25 properties is indeed achieved in a easy manner without producing any disadvantages and especially without any antagonisms between the achieved effects.

The method according to the present invention is characterized in that
30 into the cement slurry is incorporated insoluble particulate additives so that their combination with each other and with the other slurry particulate components, especially with the cement particles, will produce a size range distribution which will deeply change in an unexpected way numerous slurry essential properties.

35 Most preferably, said particulate additives are of mineral type. The mineral additives are most preferred because of their low cost and their positive effect on the environment. However, the present invention can also

use plastic wastes or other wastes, obviously to be crushed according to the expected size range. As a secondary consideration, this may have a beneficial effect on the environment by disposing in the ground (obviously controlled) wastes which can not be degraded and otherwise which should be put in a waste disposal area.

In the state of the art, additions of particulate minerals to a cement slurry have been already carried out, as well known, in the civil engineering domain, in order to improve the compressive strength. Among others, the article of F. de Larrard published in "Cement and Concrete Research" vol 19, p.161-172, 1989, will be cited. No comparison can not be obviously stated between the required properties of a civil engineering cement and those required for a "petroleum" cement.

Especially, neither the above mentioned temperature and pressure cycles nor the above mentioned requirements of rheology and of strict density control are met in the civil engineering applications. Likewise, there is no comparison at all between the civil engineering application requirements for free water or fluid loss and the considered applications, as well as the consequences of a deficiency. Thus, the above mentioned article doesn't even mention these properties. Moreover, most of the oilwells cement requirements are not required for civil engineering cement, or they are very lower according to a very different magnitude. Finally, in the civil engineering applications, the size range requirements are very rough (concrete, mortar).

Particulate additives have been also added to oilwells cements, especially to make heavy or lighten the cement (adjustment of the slurry density).

In this case, the size range is not taken into account, or the recommended size range is the opposite of which the present invention recommends.

However, some conditions, in the oilwells cement domain, exist for which a mineral additive having a particular size range have been tried to be incorporated.

Thus, attempts have been carried out in order to incorporate micro-silica, micro-barium hydroxide ("blanc fixe") or "micronic" manganese oxide (about micron size).

Low cost minerals (ashes etc...) have been also tried to be incorporated, but, in this latter case, without any size range preoccupations.

In the oilwells cements, it has been also known how to use particulate additives such as barium hydroxide or silica flour, or microsilica or agglomerated colloidal silica but their size range is substantially equal to cement size range, or such as hematite of which the size range is just larger than the cement one.

Moreover, in the state of the art, it must be noted that, indeed, substantially all sensitive properties of a oilwells slurry, especially rheology, fluid loss control and settling, have been controlled up to now (with the above indicated limits) with the help of organic additives.

These additives set a serious problem which has been well known in the art and which is that most of them have a simultaneous and contradictory action on a given property or simultaneously on several properties.

For example, a dispersing agent lowers the viscosity but improves the settling. A fluid loss control agent obviously lowers the fluid loss but increases the viscosity. Moreover, most of recently known and used additives also have an influence on the cement hydration mechanism and then, among others, on the thickening time (TT).

It has been also known that the efficiency range of such additives is often narrow due to an important sensitivity to temperature, to ion concentration (salts) of the interstitial water, etc.... Despite long and expansive developments, the result is often a formulation which is suitable only for that temperature and/or that salinity, etc....

This has been admitted in the prior art for several decades. Thus, the number of additives has been multiplied with generally specific conditions of use for each one. In order to mitigate the disadvantages of the more and more important complexity of the possible solutions, numerous softwares have been developed. These softwares only point out the chemical formulation complexity, and make easier the management of this complexity, but without solving the disadvantages.

In a surprising manner, the present invention removes the complexity.

For the first time since several decades, instead of combining together more and more additives which are more and more complex, it has been discovered that numerous essential properties could be met by reasoning in terms of selections and combinations of (preferably mineral) particulate products having different size ranges.

Such (mineral) products used according to the present invention are especially silica, hematite (or other iron oxide), barium hydroxide, and also carbonates, alumina etc..., plastic wastes and other obviously compatible wastes. Especially, the choice could be determined by, for example, the density to achieve. It has been discovered that, by using most often a selected combination of several size ranges of this type combined with the size range of the cement, a converging set of favorable properties have been spontaneously achieved, providing that the size ranges of the considered products are selected, as well as their respective proportions, in order to work at the maximum PVF, or as close as possible (taking into account other stresses such as density or water/cement ratio) to this maximum PVF (PVF being the Packing Volume Fraction), of course according to the selected size ranges and also providing that the proportion of solid matters in relation to the mixing water is selected so that the slurry is located in the hindered settling state. It is known that, in such a state, solid particles behave "collectively" like a porous solid material, the percentages of the different fractions being the same from the top to bottom of the column. On the contrary, out of this state, the different size particles or different density particles whose size is neighbouring will settle separately with different speeds. This hindered settling state corresponds, in practice, to much higher solid matter concentrations in the slurry than that admitted in the prior art.. It has been discovered a high solid matter concentration threshold beyond which the hindered settling state appears. This threshold depends of course of the chosen size ranges.

It is important to mention that such concentrations that had been judged impossible to use in the prior art (serious problems of too high viscosity and mixability) are usable according to the invention thanks to the choice of conditions that are close to the PVF max.

The invention consists therefore of the combination of three momentous features :

a) use of at least three particulate materials that are insoluble in a preferably aqueous medium, and preferably mineral, one at least of these being an oil cement or a comparable hydraulic binder, the (at least) three size ranges being "disjointed" (see further description)

and

66262-141

7

b) the choice of the proportions in the solid matters defined at a), in relation to the liquid, preferably water, or "mix water" so that the achieved fluid should be located in the hindered setting state.

5 and

c) the choice of the proportions in the solid matters defined at a), between each other, and as a function of their respective size ranges, so that the operations are run at the PVF max of the whole of the considered particles,
10 or as close as possible to the PVF max.

In a preferred embodiment, the invention provides, a cement slurry for cementing oil, water, gas or geothermal wells, comprising a mixing fluid and an insoluble particulate mixture comprising at least three size-
15 distinctive particulate materials selected from a group consisting of: (i) very large particles having an average particle size greater than 1 mm; (ii) large particles having an average particle size of from 200-800 μm ; (iii) medium particles having an average particle size of from 10-20 μm ;
20 (iv) fine particles having an average particle size of from 0.5-10 μm ; (v) very fine particles having an average particle size of from 0.05-0.5 μm ; and (vi) ultra-fine particles having an average particle size of from 7-50 nm; wherein at least one of the selected particulate material
25 comprises medium particles of a binder, at least one of the selected particulate material is of an average dimension less than that of the binder, the relative proportions of the size-distinctive particulate materials are such that the Packing Volume Fraction of the particulate mixture is
30 maximum for the selected combination of solid materials and the concentration of solid particulate materials in the mixing fluid is such that the slurry exhibits a hindered

66262-141

7a

settling state, where the solid particles behave collectively like a porous solid material.

It has been seen that "hindered settling" threshold has never been neither reached nor approached in the prior art of the oil cement. On the contrary, those skilled in the art used to take care in order to remain to solid matter concentrations that were low enough to be sure to avoid the foreseeable serious problems, due to the far too high foreseeable viscosity and the high sensitivity of the properties, especially the viscosity, towards the liquid content, sensitivity that of course, those skilled in the art always try to reduce.

Concerning the criterion in relation to the PVF, its importance has never been mentioned in the general prior art of particulate materials. Thus, the rheology, the free water, the settling, the fluid loss control, the compressive strength, the mixibility and the permeability have been favourably and simultaneously improved, and all this without substantially needing to use conventional organic additives.

Indeed, the present invention consists of, and allows, combining the above sizes to very favorable values, by combining mineral materials of different, appropriately selected, size ranges with the size range of the cement, after what an accurate adjustment of properties is able to be carried out by adding only small quantities of conventional organic additives.

The means of the present invention radically deviates from all the prior art teachings which have been accumulated and used since several decades with the above mentioned results, and moreover, the installed routine has implied the definition of precise standards such as, for example, API (American Petroleum Institute) for the barium

66262-141

7b

hydroxide and the hematite, from which the present invention also deviates. Contrary to the prior art which consists of adding, in very precise rare cases of applications, fine particles such as micro-silica with the known disadvantage
5 of the increase of the viscosity and of the effect on the cement hydration, the present invention uses

(in the above mentioned specific conditions) particles of which dimensions can be large. In the prior art, particles of large diameter have never been added, the general opinion being that a classic differential settling would occur.

5 This is really the case if prior art teachings are applied, for which only two particle sizes are very generally associated. Without being limited by any theory, it seems that the constant prior art has never achieved to master a too important number of parameters which occur in rheology etc... when there are more than two size ranges.

10 On the contrary, the present invention is based on a radically opposed concept, called below "multimodal". This concept has allowed mixing simultaneously more than two different size ranges including large dimensions. The result has been that, provided that at least a small quantity of fines had been mixed, and that the three above criterions have been
15 respected at the same time, no significant settling occurred, but, moreover, in a very unexpected manner, all the slurry essential properties were really improved without any use of conventional additives.

The "multimodal" concept (as well as its optimal realization which consists of the "multicontinuity" of particulate phases) according to the present
20 invention will be more explained from the following detailed description.

It is linked to the above mentioned PVF feature and is based first on the use of large dimension mineral particles (the "large"). As above mentioned, this absolutely goes against the constant teaching of the oil industry prior art.

The present invention has overcome this prior art technical "bar" by
25 simultaneously using fine (mineral) particles (the "fines") and it has been discovered that the "large", the cement ("medium") and "fines" cooperation stabilized the fluid instead of producing the expected disadvantages (settling, viscosification⁹) according to the prior art teaching. The invention, according to the three above features, even makes it possible to incorporate "very large"
30 particles.

Moreover, the invention makes it possible, in some cases, as it will be further established, even not to use oil cement any more.

In any cases, the invention significantly reduces the cost of oil cement slurries, which is an imperative that has never been reached for about ten
35 years in oil industry. Obviously, once this "multimodal" concept had been stated, the different combinations between the cement, one or several "fines",

one or several "larges", or the like, have been tried to be multiplied. All the results have been convergent.

According to the above principle of the present invention, which consists of incorporating the "large" particles combined with "fine" and possibly "very fine" particles, it has been noted that a "trimodal" combination of the further type (not by way of limitation) :[~]

- cement (average dimension = 10 - 20 micrometers)
- "fine" (average dimension = 1 micrometer)
- "very fine" (average dimension = 0.1 - 0.15 micrometers)

already allowed the almost perfectly achievement of all above mentioned advantages. The absence of conventional additives should be obviously noted. It seems that, in this case, the cement functions as "large" particle.

However, a "tetramodal" combination of the further type (also not by way of limitation) :

- "large" (average dimension about 200-350 micrometers)
- "medium" cement (average dimension = 10 - 20 micrometers)
- "fine " (average dimension = 1 micrometer)
- "very fine" (average dimension = 0.1 - 0.15 micrometer)

furthermore improves all of the desired properties.

Moreover, the addition of large or very large particles such as sand allows, in a spectacular manner, the slurry cost reduction which the industry has tried to achieve uncessfully since about ten years.

It has also been surprisingly noticed that, in spite of the desired very strong solid matter concentration according to the invention, the mixability was considerably improved. In fact, it is known to be an essential property of the oil cement slurries, which is standardized among others by the API.

Other essential asset, the invention makes it possible to reduce the rheology sensitivity to external features (such as for example fluid loss or water income etc...)

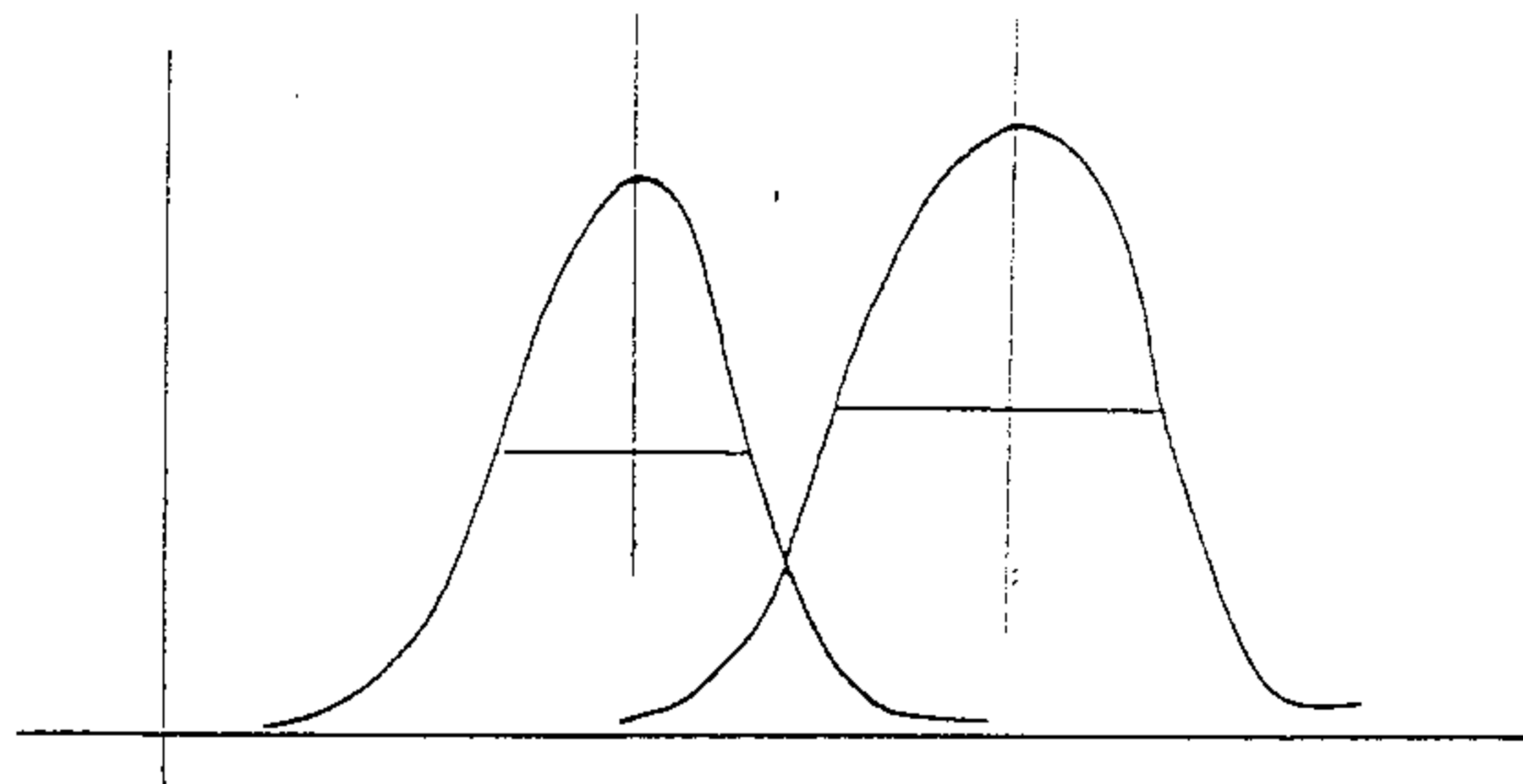
Indeed, the cement slurry placed in the annulus undergoes physio-chemical exchanges with the mediums that encircle it. It is the well known slurry "dehydrating" or "bridging" hazard that of course makes it lose all its important properties. This hazard is of course all the higher as the solid matter concentration is high.

It is one of the reasons why, in the prior art, it was used never to work at high solid matter concentrations, in order to minimize this risk.

On the contrary, the invention works above the settling threshold that leads to the hindered settling state. The well established prior art used to teach that a very high dehydrating risk should then appear. On the contrary, it never occurs thanks to the PVF max criterion. The invention improves therefore also the safety of the operations

The "tetramodal" mode will be generally preferred to the "trimodal" mode. An essential characteristic which has to be respected is that the used size ranges do not widely overlap each other.

In practice, it can be roughly considered that the criterion which has to be respected is that the size range curves have an "offset" of at least a half-peak distance as below depicted.



This criterion can be then roughly symbolized by the "disjointed size ranges" notion which will be used below for more clarity.

For example, very good results have been achieved with a "offset" ratio of about 5 to 50 and preferably about 10 between each average dimension, as according to the tri and tetramodal above examples but not by way of limitation.

Obviously, a "pentamodal" mode etc... produces results which are at least as interesting as the results given by a tetra or even tri-modal mode. However, the additional property profit is linked with additional complexity, and these modes, though they are realizable and usable, will be less preferred except for some very particular applications.

The further combinations will also be cited (according to the above mentioned criterions) between the further categories (not by way of limitation) :

- "very large", for example glass maker sand, crushed wastes (average dimension > 1 mm) and/or

- "large", for example sand or crushed wastes (average dimension = 200-800 μm) and/or

- "medium" like a material such as cement or an other hydraulic binder, or crushed wastes (average dimension 10-20 μm) and

5 - "fine" like, for example, a microcement, or some micro fly ashes or some other micro slags (average dimension 0,5 μm) and/or

- "very fine" like, for example, a latex or some pigments or some polymer microgels like a usual fluid loss control agent (average dimension 0.05-0.5 μm) and/or

10 - "ultra fine" like some colloidal silica or aluminium, etc... (average dimension 7-50nm).

- "ultra fine" particles are only used for example in the cases where an extreme stoppage or plugging is desired in an aggressive medium, and for example at a high temperature, when cost is not the most important feature.

15 In many cases, it will be possible to avoid the use of "very fine" particles. Indeed, the further improvement in the properties, which is brought about by adding "very fine" particles, could be economically unprofitable, especially as far as the filtrate control is concerned. It will be noted that this is possible only thanks to the already momentous improvement achieved according to the invention by a combination that doesn't include any "very fine" particles, the
20 said improvement making it possible to content oneself with very weak amounts of costly organic additives.

In practice, as will be shown by the further examples the main part of usual cementing can be achieved (always with respect for the three basic
25 aforementioned criterions) with combinations of the type (not by way of limitation) :

- very large
- large
- medium (for example, cement)

30 - fine

or

- large
- medium (for example, cement)
- fine

35

or

- large
- medium (crushed wastes)

- fine (microcement)

or

- large

- medium (crushed wastes)

5 - fine (micro fly ash, etc...)

and other combinations that will appear obvious for those skilled in the art
In the very last case, the cement absence will be noted.

10 According to one embodiment, the present invention generally consists of the combination of :

15 A - "Large" particles having an average dimension of about 100 - 300, preferably 200 micrometers, selected for example among sand, silica, carbonate, barium hydroxide, hematite, or other iron oxides, carbon, sulfur, and some crushed plastic industrial wastes or others.

B - "Medium" particles (about 10 - 20 micrometers), like for example an oil cement

C - "Fine" particles (about 1 micrometer) selected among :

- 20
- the carbonates (marble, chalk, calcite²)
 - the barium hydroxide ("Blanc fixe")
 - the hematite and other iron oxides
 - the silica, the carbon, the sulfur or the like
 - and some fine industrial wastes.

25 D - "Very fine" particles (about 0.1 micrometer) as for example a latex, a silica condensate (silica fume) or a condensate of manganese oxide fumes.

30 The fields of relative proportions for the different kinds of particulate materials won't be given here. Indeed, these percentages of A, B, etc... must be established according to the achievement criterion of the PVF max or a PVF as close as possible to the PVF max. It will be remained that the calculation of the PVF is known and usual. It is based on known equations including a "cutting" of each size range of each component of the particulate blending. In the further examples, the PVF values have been achieved by

35 dividing each size range curve of each component into 31 "fractions".

As it has been seen, it will also be very profitable to use "very large" particles (>1 mm) and, in the cases for which the technical problems to be

solved are extreme, "ultra fine" particles. A particularly profitable combination will be of the "trimodal" type :

- large sand (glass maker sand) 350 micrometers
- material (some crushed industrial wastes) 10-20 micrometers
- 5 - microsilica or industrial wastes 0,5-3 micrometers, the said combination being added with a very slight amount (0.5 % in relation to the solids) of fluid loss control agent, and possibly very slight amounts of other usual organic additives, to optimize and refine the fluid properties

10 The following examples illustrate the invention without however limiting its scope.

Example 1

A cement slurry with a normal density of 15.8 ppg (1,89 g/cm³) was obtained with the following composition ("trimodal") :

- 15 - Silica (180 μ m) 23 % by weight of solids
- Cement (about 20 μ m) 51 % by weight of solids
- Dyckherhoff API classe "G"
- Tropical version "Gulf"
- 20 - Barium hydroxide ("Blanc fixe") (about 1 μ m) 26 % by weight of solids

(all the particle dimensions are average values)

A porosity of 59 % was obtained, and the further rheology after mixing was obtained :

- 25 PV = 25 cP
- Ty = 57 lb/100 Sqft (27,3 Pa)

It has been noted that, without any chemical additives, the rheology is already comparatively low and then is correct.

Free water : 0

30 Compressive strength : 3300 psi (23 MPa) after 24 h. at 185°F (85°C).

Example 2

A lightened cement slurry with a density of 12 ppg (1,44 g/cm³) was obtained with the following composition ("trimodal") :

- 35 - Crushed plastic wastes (300 μ m) 24 % by weight of solids
- Cement (as example 1) 50 % by weight of solids
- Fine carbonate (about 2 μ m) 26 % by weight of solids

The porosity is 56 %.

The main problem of such slurries, i.e. their well known stability defect, is solved without any chemical additives: no settling is observed.

The free water is only 3 ml/250 ml, that means about 1%, which is an excellent result.

The compressive strength is 1450 psi (10 MPa) after 24 h. at 185°F (85°C)

10 Example 3

A heavy cement slurry with a density of 19 ppg (2,1 g/cm³) was obtained with the following composition ("trimodal") :

- 15 - Large hematite (300 μm) 58 % by weight of solids
- Cement (as example 1) 20 % by weight of solids
- Industrial Waste of iron oxide type (about 2 μm) 22 % by weight of solids

The porosity is 57 %.

20 The rheology after mixing is :

PV = 15 cP Ty = 6 lb/100 sqft (2,9 Pa)

The compressive strength after 24 h. at 185°F (85°C) is 2180 psi (15 MPa)

25

Example 4 : Mixability tests.

30 Different cement slurries have been prepared according to the API standards, with a basis of "Dyckherhoff" cement API class G, Tropical version ("Gulf").

The slurries have been submitted to the mixability test, according to the API standards.

35 The compositions, properties and results are gathered in the further Table I.

For each test, a comparison was made between a slurry constituted according to the prior art methods, namely without respecting the three above

criteria, and by trying to increase the solid matter contents, and a slurry constituted according to the invention. The comparative slurries are clearly impossible to mix, whereas on the contrary, the slurries according to the invention are clearly mixable.

5 This is quite surprising while taking into account the additives added, and the proportions thereof.

The tests n° 6 et 8 will be particularly noticed.

10 The test n° 5 (35 % by weight of silica in relation to the cement) corresponds to a slurry that is usually known in the prior art as impossible to use because it is in practice impossible to mix, except in presence of a great amount of a usual distributing agent.

15 On the contrary, in the test n° 6 according to the invention which contains the same proportion of silica, and has the same density and the same solids/liquid ratio, the size range choice according to the invention criteria leads to a slurry that can be quite easily mixed and cast without any distributing additive.

20 As far as the last test (n° 8) is concerned, the optimization of the PVF makes it possible, by incorporating 85 % of silica, to obtain a mixable slurry to a high density, where as at this same density the classic silica flour-based composition is impossible to mix.

Example 5: Tests with fine iron oxide.

25 As indicated in the first part of the further Table II, slurries were prepared of "Dyckerhoff" Cement Class G API Tropical Version "Gulf". The achieved densities are also mentioned.

The test results are gathered in the second part of Table II.

30 An excellent slurry stability will be noticed, particularly while considering the low rheology values.

Among others, the n° 8 test shows an almost complete lack of settling (cf Δp) and free water for a slurry whose shearing threshold T_y and plastic viscosity are very low.

35 As to test n° 1, it shows that at an extremely high density, the invention still makes it possible to define a perfectly pumpable fluid.

Example 6

The slurry n° 9 of Table II was took up again

5	Cement	47 % by weight of solids
	Silica (180 μm)	26 % by weight of solids
	Iron oxide (2 μm)	27 % by weight of solids

and this slurry has been tried to be optimized by very little additive amounts :

- 10
- fluid loss control agent of type acrylic terpolymer :
0,91 % by weight of cement.
 - setting retarder aagent of type lignosulfonate :
0,14 % by weight of cement.

15 At 185°F*, the setting time is 6 h 50 min and the API fluid loss is 111 ml after 30 minutes.

This example shows that the invention makes it possible to obtain a slurry whose properties are good with only little usual additive amounts, therefore at low cost.

20 * (85°C)

25

30

35

TABLE I

Test	Particulate additive *	concentration % BWOC	density in g/cm ³ (ppg)	PVF	porosity %	solid/liquid ratio	mixability
1	FS	35	2.04 (17)	0.732	48.34	1.075	NO
2	SA	35	2.04 (17)	0.765	48.34	1.075	YES
3	FS HE	60 4.78	2.04 (17)	0.740	47.62	1.105	NO
4	SA RI	60 4.155	2.04 (17)	0.787	47.62	1.105	YES
5	FS HEM	35 25.7	2.16 (18)	0.740	47.62	1.106	NO
6	SA RI	35 21.69	2.16 (18)	0.802	47.62	1.106	YES
7	FS HEM	35 63.21	2.28 (19)	0.749	47.62	1.105	NO
8	SA RI	85.1 91.36	2.28 (19)	0.847	47.62	1.105	YES

FS = silica flour (20 micrometers) - SA = sand (180 micrometers) - HE = hematite (100 micrometers)
RI = industrial wastes of type iron oxides (about 2 micrometers) - BWOC = by weight of cement

TABLE II(1)

Test	Cement (fraction in volume)	silica 180 micrometers (fraction in volume)	iron oxide 2 micrometers (fraction in volume)	density	
				(ppg)	(g/cm ³)
1	0.3	0.2	0.5	21.81	2.62
2	0.7	0.2	0.1	17.88	2.15
3	0.3	0.65	0.05	16.45	1.98
4	0.7	0.25	0.05	17.29	2.08
5	0.5	0.2	0.3	19.85	2.39
6	0.3	0.425	0.275	19.13	2.30
7	0.7	0.225	0.075	17.59	2.11
8	0.5	0.45	0.05	16.87	2.03
9	0.5	0.325	0.175	18.36	2.21

Preparation of the slurries

- API mixing conditions
- porosity 50 %
- 295, 14g of water and 6g of distributing agent of type polynaphthalene sulfonate

TABLE II (2)

Test	T 1bf/100sqft	y + Pa	Pv cp	1bf/100sqft	Ty * Pa	Pv * cp	ΔP 1b/gal	(o) g/cm3	free water ml/250 ml
1	84.3	40.3	127	121	57.9	196	0	0	0.3
2	9.8	4.7	45.4	22.9	10.9	63	0.5	0.06 +	2
3	0.2	0.1	22.1	1.1	0.5	7.0	1.7	0.20	28
4	6.2	2.3	44.4	12.9	6.17	52	0.7	0.08	2
5	28.2	13.5	46.8	42.8	20.5	79	0.1	0.01	1
6	7.5	3.6	27.8	10.4	5	30.6	0.7	0.08	2
7	6.5	3.1	46.1	15.1	7.2	52.1	0.5	0.06	2
8	0.9	0.4	28.3	5.2	2.5	27.7	1.1	0.13	1
9	7.9	3.8	29.6	13.9	6.7	37.6	0.5	0.06	3.5

(+) after mixing
 (*) after 20 min at 80° F (27° c)
 (o) "BP" Test : The density difference is measured between the top and the basis of a cement column

66262-141

20

CLAIMS:

1. A cement slurry for cementing oil, water, gas or geothermal wells, comprising a mixing fluid and an insoluble particulate mixture comprising at least three size-
5 distinctive particulate materials selected from a group consisting of:

(i) very large particles having an average particle size greater than 1 mm;

(ii) large particles having an average particle
10 size of from 200-800 μm ;

(iii) medium particles having an average particle size of from 10-20 μm ;

(iv) fine particles having an average particle size of from 0.5-10 μm ;

(v) very fine particles having an average
15 particle size of from 0.05-0.5 μm ; and

(vi) ultra-fine particles having an average particle size of from 7-50 nm;

wherein at least one of the selected particulate material
20 comprises medium particles of a binder, at least one of the selected particulate material is of an average dimension less than that of the binder, the relative proportions of the size-distinctive particulate materials are such that the Packing Volume Fraction of the particulate mixture is
25 maximum for the selected combination of solid materials and the concentration of solid particulate materials in the mixing fluid is such that the slurry exhibits a hindered settling state, where the solid particles behave collectively like a porous solid material.

66262-141

21

2. The cement slurry according to claim 1, wherein the mixing fluid is water.

3. The cement slurry according to claim 1 or 2, wherein the very large particles are of glass maker sand or
5 crushed waste.

4. The cement slurry according to any one of claims 1 to 3, wherein the large particles are of sand, silica, carbonate, barium hydroxide, an iron oxide, a carbon, a sulfur or crushed waste.

10 5. The cement slurry according to claim 4, wherein the iron oxide is hematite.

6. The cement slurry according to claim 4, wherein the crushed waste is crushed industrial waste.

7. The cement slurry according to any one of
15 claims 1 to 6, wherein the medium particles are a binder or of crushed waste.

8. The cement slurry according to claim 7, wherein the binder is a hydraulic material.

9. The cement slurry according to any one of
20 claims 1 to 8, wherein the binder is cement.

10. The cement slurry according to claim 9, wherein the cement is an oil cement.

11. The cement slurry according to any one of claims 1 to 10, wherein the fine particles are of slag or
25 fly ash.

12. The cement slurry according to any one of claims 1 to 10, wherein the fine particles are of a microcement.

66262-141

22

13. The cement slurry according to any one of claims 1 to 10, wherein the fine particles are of a carbonate, barium hydroxide, an iron oxide, a silica, a carbon, a sulfur or an industrial waste.

5 14. The cement slurry according to claim 13, wherein the carbonate is marble, chalk or calcite.

15. The cement slurry according to claim 13, wherein the iron oxide is hematite.

10 16. The cement slurry according to any one of claims 1 to 15, wherein the very fine particles are of polymer, a silica condensate, or a condensate of manganese oxide fumes or are a pigment.

17. The cement slurry according to claim 16, wherein the polymer is latex.

15 18. The cement slurry according to claim 16, wherein the polymer is a polymer microgel for use as a fluid loss control agent.

19. The cement slurry according to claim 16, wherein the silica condensate is a silica fume.

20 20. The cement slurry according to any one of claims 1 to 19, wherein the ultra-fine particles are of a colloidal well dispersed silica or alumina.

25 21. The cement slurry according to any one of claims 1 to 20, wherein the solid particulate mixture consists of very large, large, medium and fine particulate materials.

22. The cement slurry according to any one of claims 1 to 20, wherein the solid particulate mixture

66262-141

23

consists of very large, medium and fine particulate materials.

23. The cement slurry according to claim 21 or 22, wherein the solid particulate mixture further consists of
5 very fine particles.

24. The cement slurry according to any one of claims 21 to 23, wherein the solid particulate mixture further consists of ultra-fine particles.

25. The cement slurry according to any one of
10 claims 1 to 24, further comprising one or more additives useful for oilfield cementing.

26. The cement slurry according to claim 1, wherein the solid particulate mixture consists of:

24%, by weight of the solids, of crushed plastic
15 wastes (about 300 μm),

50%, by weight of the solids, of oil cement (about 20 μm), and

26%, by weight of the solids, of fine carbonate (about 2 μm), with a density of 12 ppg (1,44 g/cm³).

20 27. The cement slurry according to claim 1, wherein the solid particulate mixture consists of:

23%, by weight of the solids, of silica (about 180 μm),

51%, by weight of the solids, of oilfield cement
25 (about 20 μm), and

26%, by weight of the solids, of barite (feed white - about 1 μm) with a density of 15,8 ppg (1,89 g/cm³).

66262-141

24

28. The cement slurry according to claim 1, wherein the solid particulate mixture consists of:

58%, by weight of the solids, of large hematite (about 300 μm),

5 20%, by weight of the solids, of oilfield cement (about 20 μm), and

22%, by weight of the solids, of industrial waste of type iron oxide (about 2 μm), with a density of 19 ppg (2,1 g/cm³).

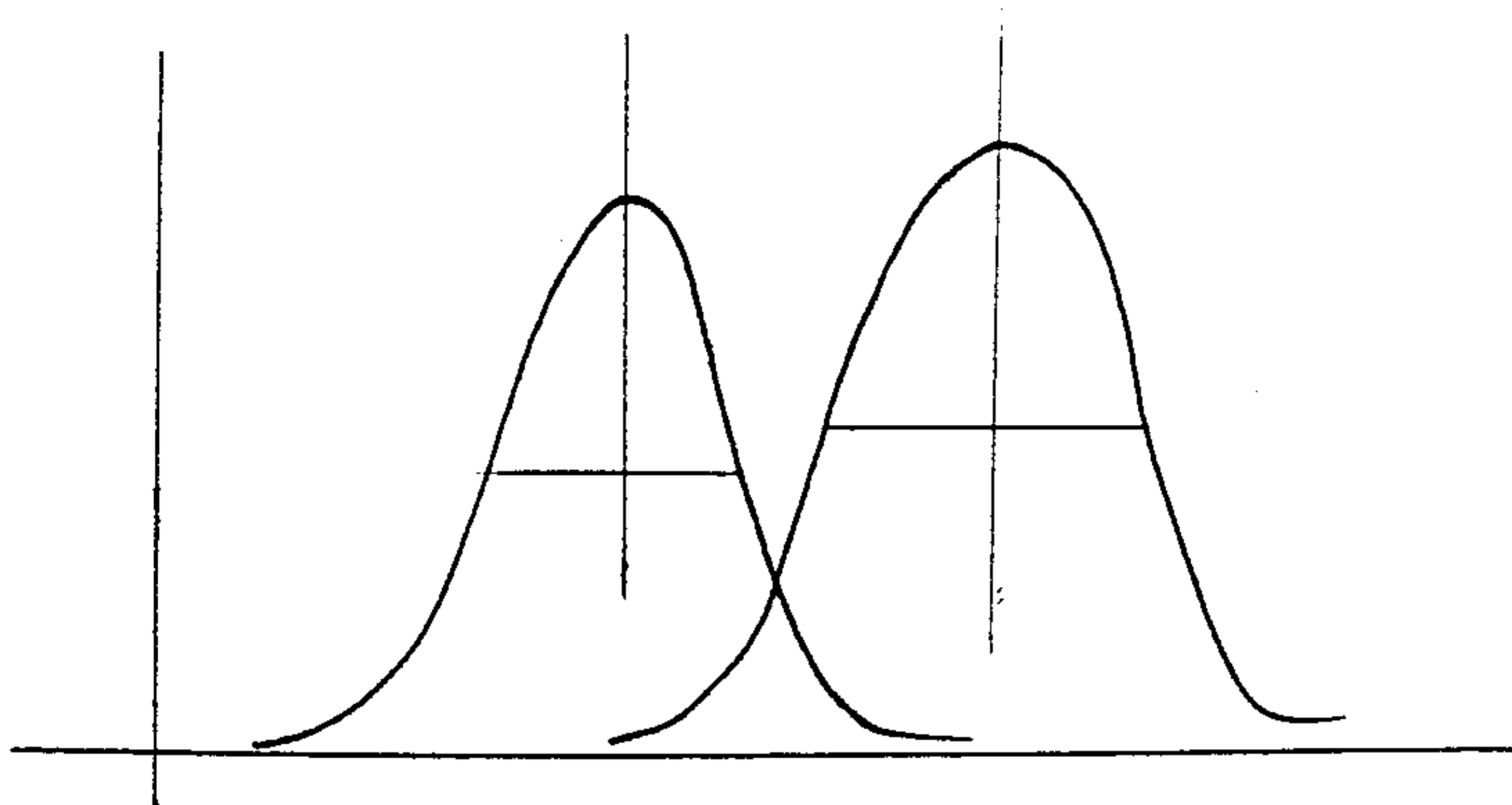
10 29. A method of cementing oil, gas, water, or geothermal wells comprising injecting a slurry according to any one of claims 1 to 28 into the well.

SMART & BIGGAR

OTTAWA, CANADA

PATENT AGENTS

CA2117276



*Patent Agents
Smart & Bigman*