

**(12) PATENT**  
**(19) AUSTRALIAN PATENT OFFICE**

**(11) Application No. AU 200062702 B2**  
**(10) Patent No. 772997**

(54) Title  
**A low-density and low-porosity cementing slurry for oil wells or the like**

(51)<sup>7</sup> International Patent Classification(s)  
**C04B 028/02 C04B 028/08**  
**C04B 007/02 C04B 038/08**  
**C04B 022/14 E21B 033/13**

(21) Application No: **200062702**

(22) Application Date: **2000.07.06**

(87) WIPO No: **WO01/09056**

(30) Priority Data

(31) Number	(32) Date	(33) Country
<b>99/09847</b>	<b>1999.07.29</b>	<b>FR</b>

(43) Publication Date : **2001.02.19**

(43) Publication Journal Date : **2001.05.03**

(44) Accepted Journal Date : **2004.05.13**

(71) Applicant(s)  
**Sofitech N.V.**

(72) Inventor(s)  
**Bruno Drochon; Andre Garnier**

(74) Agent/Attorney  
**Griffith Hack,GPO Box 1285K,MELBOURNE VIC 3001**

(56) Related Art  
**US 3804058**  
**US 5571318**

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
8 February 2001 (08.02.2001)

PCT

(10) International Publication Number  
**WO 01/09056 A1**

(51) International Patent Classification<sup>7</sup>: **C04B 28/02**,  
E21B 33/13, C04B 28/08 // (C04B 28/02, 7:02, 22:14,  
38:08), 201:20

[FR/FR]; 8, place Georges Pompidou, F-93160 Noisy Le  
Grand (FR). **GARNIER, André** [FR/FR]; 1, avenue du  
Colonel Fabien, F-78210 Saint Cyr l'Ecole (FR).

(21) International Application Number: PCT/EP00/06459

(74) Agent: **MENES, Catherine**; Etudes et Productions  
Schlumberger, Intellectuel Property Department, 26, rue  
de la Cavée, Boîte postale 202, F-92142 Clamart Cedex  
(FR).

(22) International Filing Date: 6 July 2000 (06.07.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
99/09847 29 July 1999 (29.07.1999) FR

(81) Designated States (*national*): AL, AM, AT, AU, AZ, BA,  
BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES,  
FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,  
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG,  
MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE,  
SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN,  
YU, ZW.

(71) Applicant (*for all designated States except CA, FR, US*):  
**SOFITECH N.V.** [BE/BE]; Rue de Stalle ~~142~~ B-1180  
Brussels (BE). ~~140~~

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,  
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for CA only*): **SCHLUMBERGER CANADA  
LIMITED** [CA/CA]; 24th floor, Monenco Place, 801 6th  
Avenue, S.W., Calgary, Alberta T2P 3W2 (CA).

(71) Applicant (*for FR only*): **COMPAGNIE DES SER-  
VICES DOWELL SCHLUMBERGER** [FR/FR]; 50,  
avenue Jean-Jaurès, F-92541 Montrouge (FR).

**Published:**  
— *With international search report.*

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **DROCHON, Bruno**

*For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.*

(54) Title: A LOW-DENSITY AND LOW-POROSITY CEMENTING SLURRY FOR OIL WELLS OR THE LIKE

(57) Abstract: The invention relates to a cement slurry for cementing an oil well or the like, the slurry having a density lying in the range 0.9 g/cm<sup>3</sup> to 1.3 g/cm<sup>3</sup>, and being constituted by a solid fraction and a liquid fraction, having porosity (volume ratio of liquid fraction over solid fraction) lying in the range 38 % to 50 %. The solid fraction is constituted by a mixture of lightweight particles, microcement and optionally portland cement and gypsum. Such cements have remarkable mechanical properties due to their very low porosity in spite of having very low density.



WO 01/09056 A1

## A LOW-DENSITY AND LOW-POROSITY CEMENTING SLURRY FOR OIL WELLS OR THE LIKE

The present invention relates to drilling techniques for oil wells, gas wells, water wells, geothermal wells, and the like. More precisely, the invention relates to cementing slurries of low density and low porosity.

After an oil well or the like has been drilled, casing or coiled tubing is lowered down the borehole and is cemented over all or part of its height. Cementing serves in particular to eliminate any fluid interchange between the various formation layers that the borehole passes through, preventing gas from rising via the annulus surrounding the casing, or indeed it serves to limit ingress of water into a well in production. Naturally, another main objective of cementing is to consolidate the borehole and to protect the casing.

While it is being prepared and then injected into the well so as to be placed in the zone that is to be cemented, the cementing slurry must present relatively low viscosity and it must have rheological properties that are practically constant. However, once it is in place, an ideal cement would rapidly develop high compression strength so as to enable other work on the well that is being built to start again quickly, and in particular so as to enable drilling to be continued.

The density of the cement must be adjusted so that the pressure at the bottom of the well compensates at least for the pore pressure in the geological formations through which the well passes so as to avoid any risk of eruption. As well as this lower limit on density, there is also an upper limit. This upper limit is that the hydrostatic pressure generated by the column of cement plus the head losses due to the circulation of the fluids being pumped must remain below the fracturing pressure of the rocks in the section being cemented. Certain geological formations are very fragile and require densities close to that of water or even lower.

The risk of eruption diminishes with column height so the density required for compensating pore pressure is then lower. In addition, cementing a large height of column is advantageous since that makes it possible to  
5 reduce the number of sections that are cemented. After a section has been cemented, drilling must be restarted at a smaller diameter, so having a large number of sections requires a hole to be drilled near the surface that is of large diameter, thereby giving rise to excess cost due to  
10 the large volume of rock to be drilled and due to the large weight of steel required for the sections of casing, given their large diameters.

All of those factors favor the use of cement slurries of very low density.

15 The cement slurries in the most widespread use have densities of about  $1900 \text{ kg/m}^3$ , which is about twice the density desired for certain deposits. To lighten them, the simplest technique is to increase the quantity of water while adding stabilizing additives (known as  
20 "extenders") to the slurry for the purpose of avoiding particles settling and/or free water forming at the surface of the slurry. Manifestly, that technique cannot get down to a density close to  $1000 \text{ kg/m}^3$ . Furthermore, hardened cements formed from such slurries have greatly  
25 reduced compression strength, a high degree of permeability, and poor adhesive capacity. For these reasons, that technique cannot be used to go below densities of about  $1300 \text{ kg/m}^3$  while still conserving good isolation between geological layers and providing  
30 sufficient reinforcement for the casing.

Another technique consists in lightening the cement slurry by injecting gas into it (generally air or nitrogen) before it sets. The quantity of air or nitrogen added is such as to reach the required density.  
35 It can be such as to form a cement foam. That technique provides performance that is a little better than the preceding technique since the density of gas is lower

than that of water, so less needs to be added. Nevertheless, in oil industry applications density remains limited in practice to densities greater than  $1100 \text{ kg/m}^3$ , even when starting with slurries that have already been lightened with water. Above a certain "quality of foam", i. e. a certain ratio of gas volume to volume of the foamed slurry, the stability of the foam falls off very quickly, the compression strength of the foam after it has set becomes too low, and its permeability becomes too high, thereby compromising durability in a hot aqueous medium which includes ions that are aggressive to a greater or lesser extent for cement.

10 US 3,804,058 and GB 2,027,687A describe the use of hollow glass or ceramic microspheres to produce low density cement slurries for use in the oil and gas industry.

Accordingly, it would be advantageous to provide cementing slurries that are more particularly adapted to cementing wells, having both low density and low porosity, and that are obtained without introducing gas. In particular, it would be advantageous for such a cementing slurry to be used in oil wells, gas wells, water well, geothermic wells or the like.

20 According to the invention, there is provided a cement slurry for cementing well having a density lying in the range  $0.9 \text{ g/cm}^3$  to  $1.3 \text{ g/cm}^3$ , in particular in the range  $0.9 \text{ g/cm}^3$  to  $1.1 \text{ g/cm}^3$ , and being constituted by a solid fraction and a liquid fraction, having porosity (volume ratio of liquid fraction over solid fraction) lying in the range 38% to 50%, and preferably less than 45%.

25 The solid fraction is preferably constituted by a mixture comprising:

- . 60% to 90% (by volume) of lightweight particles having a mean size lying in the range 20 microns( $\mu\text{m}$ ) to 350  $\mu\text{m}$ ;
- . 10% to 30% (by volume) of micro-cement having a mean particle diameter lying in the range 0.5  $\mu\text{m}$  to 5  $\mu\text{m}$ ;
- 30 . 0 to 20% (by volume) of Portland cement, having particles with a mean diameter lying in the range 20 $\mu\text{m}$  to 50  $\mu\text{m}$ ; and
- . 0 to 30% (by volume) of gypsum.

The low porosities achieved make it possible to optimize mechanical properties and permeability. By presenting mechanical properties that are much better than those of conventional lightened systems, and permeabilities that are lower, the leakproofing and adhesion properties of ultralightweight cement and the resistance of such formulations to chemical attack are thus much better than with the systems presently in use for low densities, even though the invention makes it possible to reach densities that are exceptionally low, and in particular that are lower than the density of water. In addition, slurries of the invention do not require gas, thus making it possible to avoid the logistics that would otherwise be required for manufacturing foamed cements.

The method of the invention is characterized in that particulate additives are incorporated in the cement slurry, such that in combination with one another and with the other particulate components of the slurry, and in particular with the particles of micro-cement (or comparable hydraulic binder), they give rise to a grain-size distribution that significantly alters the properties of the slurry. The said particulate additives are organic or inorganic and they are selected for their low density.

The low density is obtained by combining lightweight particles and cement (or a comparable hydraulic binder). Nevertheless, rheological and mechanical properties will only be satisfactory if the size of the particles and the volume distribution thereof is selected in such a manner as to maximize the compactness of the solid mixture.

For a solid mixture having two components (the lightweight particles and the micro-cement), this maximum compactness is generally obtained for a volume ratio of lightweight particles to micro-cement lying in the range 70:30 to 85:15, and preferably in the range 75:25 to 80:20, for lightweight particles selected to be of a size

that is at least 100 times approximately the size of the particles of micro-cement, i.e. in general, particles that are greater than 100  $\mu\text{m}$  in size. These values can vary, in particular as a function of the greater or  
5 lesser dispersion in the grain-size distribution of the lightweight particles. Particles having a mean size greater than 20 microns can also be used, but performance is not so good. Particles greater than 350 microns are generally not used because of the narrow size of the  
10 annular gaps to be cemented.

Mixtures having three or more components are preferred since they make it possible to obtain greater compactness if the mean sizes of the various components are significantly different. For example, it is possible  
15 to use a mixture of lightweight particles having a mean size of 150 microns, lightweight particles having a mean size of 30 microns, and micro-cement, at a volume ratio lying close to 55:35:10, or departing a little from these optimum proportions, the mixture being constituted by 50%  
20 to 60% (by volume) of the first lightweight particles of mean diameter lying in the range 100  $\mu\text{m}$  to 400  $\mu\text{m}$ , 30% to 45% of the second lightweight particles of mean diameter lying in the range 20  $\mu\text{m}$  to 40  $\mu\text{m}$ , and 5% to 20% of micro-cement. Depending on the application, the fraction  
25 of lightweight particles of intermediate size can be replaced by Portland cement of ordinary size, in particular class G Portland cement.

The term "micro-cement" is used in the invention to designate any hydraulic binder made up of particles of  
30 mean size of about 3  $\mu\text{m}$  and including no, or at least no significant number of, particles of size greater than 10  $\mu\text{m}$ . They have a specific surface area per unit weight as determined by the air permeability test that is generally about 0.8  $\text{m}^2/\text{g}$ .

35 The micro-cement can essentially be constituted by Portland cement, in particular a class G Portland cement typically comprising about 65% lime, 25% silica, 4%

alumina, 4% iron oxides, and less than 1% manganese oxide, or equally well by a mixture of Portland micro-cement with microslag, i.e. a mixture making use essentially of compositions made from clinker comprising  
5 45% lime, 30% silica, 10% alumina, 1% iron oxides and 5% to 6% manganese oxide (only the principal oxides are mentioned here; and these concentrations can naturally vary slightly as a function of the supplier). For very low temperature applications ( $< 30^{\circ}\text{C}$ ), Portland micro-  
10 cement is preferable over a mixture of micro-cement and slag because of its reactivity. If setting at right angles is required, plaster (gypsum) can be used for all or some of the middle-sized particles.

The lightweight particles typically have density of  
15 less than  $2\text{ g/cm}^3$ , and generally less than  $0.8\text{ g/cm}^3$ . 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  $150\text{ }\mu\text{m}$ . It is also  
20 possible to use synthetic materials such as hollow glass beads, and more particularly preferred are beads of sodium-calcium-borosilicate glass presenting high compression strength or indeed microspheres of a ceramic, e.g. of the silica-alumina type. These lightweight  
25 particles can also be particles of a plastics material such as beads of polypropylene.

In general, the density of the slurry is adjusted essentially as a function of which lightweight particles are chosen, but it is also possible to vary the ratio of  
30 water to solid (keeping it in the range 38% to 50% by volume), the quantity of micro-cement or of comparable hydraulic binder (in the range 10% to 30%), and adding Portland cement of ordinary size as a replacement for a portion of the lightweight particles.

35 Naturally, the slurry can also include one or more additives of types such as: dispersants; antifreeze; water retainers; cement setting accelerators or

retarders; and/or foam stabilizers, which additives are usually added to the liquid phase, or where appropriate incorporated in the solid phase.

Formulations made in accordance with the invention  
5 have mechanical properties that are significantly better than those of foamed cements having the same density. Compression strengths are very high and porosities very low. As a result, permeabilities are smaller by several orders of magnitude than those of same-density foamed  
10 cements, thereby conferring remarkable properties of hardness on such systems.

The method of the invention considerably simplifies the cementing operation, since it avoids any need for logistics of the kind required for foaming.

15 Slurries prepared in accordance with the invention also have the advantage of enabling all of the characteristics of the slurry (rheology, setting time, compression strength, ...) to be determined in advance for the slurry as placed in the well, unlike foamed  
20 slurries where certain parameters can be measured on the slurry only prior to the introduction of gas (setting time).

The following examples illustrate the invention without limiting its scope.

25

#### EXAMPLE 1

Low-density and low-porosity slurries can be obtained from mixtures of particles of two or three (or even more) different sizes, so long as the packing volume  
30 fraction (PVF) is optimized.

The properties of three slurries prepared in accordance with the invention are described and compared with those of a conventional low-density extended slurry and of a foamed system:

35 Slurry A: A mixture of powders was prepared. It comprised 55% by volume of hollow spheres taken from cenospheres having an average size of 150 microns

(specific gravity 0.75); 35% by volume of glass microspheres having an average size of 30 microns; and 10% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

5       The microspheres used are sold by 3M<sup>TM</sup> under the name Scotchlite S60/10,000; such microspheres have a density of 0.6 g/cm<sup>3</sup> and a grain-size distribution such that 10% of the particles (by volume) have a size of less than 15  $\mu$ m, 50% less than 30  $\mu$ m, and 90% less than 70  $\mu$ m;  
10   these particles were selected in particular because of their high compression strength (90% of the particles withstand isostatic compression of 68.9 MPa or 10,000 psi).

      Water and the following additives were mixed with  
15   this powder so as to ensure that the volume percentage of liquid in the slurry was 42%: water retainer based on 2-acrylamido 2-methylpropane sulfonic acid (AMPS) at 0.2% (percent by weight of powder, i.e. all of the solid particles taken together (micro-cement, microspheres and  
20   cenospheres for this slurry A)); an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based on polynaphthalene sulfonate at 0.07 gallons per bag of powder. It should be observed that a bag of powder is defined by analogy with bags of cement as being  
25   a bag containing 45.359 kg of mixture, in other words 1 gpb = 0.03834 liters (/) of additive per kg of mixture.

Slurry B: A mixture of powders was prepared. It comprised 78% by volume of hollow spheres obtained from cenospheres having a mean size of 150 microns and a  
30   density of 0.63 g/cm<sup>3</sup>, and 22% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

      Water and the following additives were mixed with the powder so that the volume percentage of liquid in the  
35   slurry was 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based

on polynaphthalene sulfonate at 0.1 gallons per bag of powder.

5        Slurry C: A mixture of powders was prepared. It comprised 78% by volume of Scotchlite glass microspheres having a mean size of 30 microns, and 22% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

10        Water and the following additives were mixed with said powder so that the volume percentage of liquid in the slurry was 45%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based on polynaphthalene sulfonate at 0.145 gallons per bag of powder.

15        Slurry D: A mixture of powders was prepared. It comprised 78.4% by volume of hollow spheres derived from cenospheres having a mean size of 150 microns (density 0.72 g/cm<sup>3</sup>) and 21.6% by volume of glass G Portland cement.

20        Water and the following additive were mixed with said powder so that the volume percentage of liquid in the slurry was 57%: an antifoaming agent at 0.03 gallons per bag of powder.

25        Slurry E: A conventional slurry of density 1900 kg/cm<sup>3</sup> was prepared based on a class G Portland cement.

The slurry was foamed with a quantity of foam of 50% so as to obtain a slurry whose final density was 950 kg/m<sup>3</sup>.

Slurry	A	B	C	D	E
Density	924 (7.7)	1068 (8.9)	1056 (8.8)	1130 (9.4)	950 (7.9)
Porosity	42%	42%	45%	57%	78%*
PV	87	68	65		
Ty	3.7 (7.7)	8.6 (18)	3.4 (7.2)		
CS	11.7 (1700)	19.3 (2800)	14.5 (2100)	2.48 (360)	4.62 (670)

The densities are expressed in kg/m<sup>3</sup> (and in pounds per gallon in parentheses).

Rheology is expressed by a flow threshold Ty in Pascals (and in pounds per 100

5 square inch in parentheses), and by plastic viscosity in mPa.s or centipoise, using the Bingham fluid model. These parameters were determined at ambient temperature.

CS means compression strength after 24 hours for cement set at 60°C (140°F) at a pressure of 6.9 MPa (1000 psi), and it is expressed in Mpa (and in pounds per square inch in parentheses).

10

\* In this case, porosity was calculated as volume of gas + water over total volume of the slurry.

It can be seen that for the slurries prepared in accordance with the invention,

15 compression strength is particularly high for densities that are so low and that these slurries present excellent rheology in spite of their low porosity.

## EXAMPLE 2

For slurries having a density greater than 8 pounds per gallon (ppg), a portion of the  
20 lightweight particles can be substituted by class G cement.

Slurry A: A mixture of powders was prepared. It comprised 55% by volume hollow spheres derived from cenospheres having a mean size of 150 microns, 35% by

volume of Scotchlite glass microspheres having a mean size of 30 microns, and 10% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

5        Water and the following additives were mixed with the powder so that the volume percentage of the liquid in the slurry was 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03  
10       gallons per bag of powder; and a super-plasticizer based on polynaphthalene sulfonate at 0.07 gallons per bag of powder.

Slurry B: A mixture of powders was prepared. It comprised 55% by volume of hollow spheres derived from cenospheres having a mean size of 150 microns, 25% by  
15       volume of Scotchlite glass microspheres having a mean size of 30 microns, 10% by volume of a class G Portland cement, and 10% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

      Water and the following additives were mixed with  
20       the powder so as obtain a volume percentage of liquid in the slurry of 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based  
25       on polynaphthalene sulfonate at 0.01 gallons per bag of powder.

Slurry C: A mixture of powders was prepared. It comprised 55% by volume of hollow spheres derived from cenospheres having a mean size of 150 microns, 20% by  
30       volume of Scotchlite glass microspheres having a mean size of 30 microns, 15% by volume of a class G Portland cement, and 10% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

      Water and the following additives were mixed with the powder so that the volume percentage of liquid in the  
35       slurry was 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based

on polynaphthalene sulfonate at 0.01 gallons per bag of powder.

Slurry D: A mixture of powders was prepared. It comprised 55% by volume of hollow spheres derived from cenospheres having a mean size of 150 microns, 15% by volume of Scotchlite glass microspheres having a mean size of 30 microns, 20% by volume of a class G Portland cement, and 10% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

Water and the following additives were mixed with the powder so as to obtain a volume percentage of liquid in the slurry of 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based on polynaphthalene sulfonate at 0.01 gallons per bag of powder.

Densities are expressed in  $\text{kg/m}^3$  (and in pounds per gallon in parentheses). Rheology is expressed by the flow threshold  $T_y$  in Pascals (and in pounds per 100 square feet in parentheses), and by plastic viscosity  $PV$  in  $\text{mPa}\cdot\text{s}$  or centipoise, using the Bingham fluid model. These parameters were determined at ambient temperature. CS stands for compression strength after 24 hours and after 48 hours for cement setting at  $60^\circ\text{C}$  at a pressure of 6.9 MPa (1000 psi), expressed in MPa (and in pounds per square inch in parentheses).

Slurry	A	B	C	D
Density	924 (7.7)	1068 (8.9)	1140 (9.5)	1218 (10.15)
Porosity	42%	42%	42%	42%
PV	87	90	100	109
Ty	7.7	8.8	9.0	11.2
CS (24 h)	7.58 (1100)	18.3 (2650)	19.7 (2850)	20.7 (3000)
CS (48 h)	9.0 (1300)	19.0 (2750)	29.7 (4300)	28.3 (4100)

Adding Portland cement as a portion of the "medium-sized" particles makes it possible to cover the entire  
 5 range of densities from 8 ppg to 11 ppg and significantly improves compression strength. This addition does not disturb the good rheological properties in any way.

### EXAMPLE 3

10 For slurries having a density greater than 8 ppg, a portion of the lightweight particles can be substituted by micro-cement or by a mixture of micro-cement and slag.

Slurry A: A mixture of powders was prepared. It comprised 55% by volume hollow spheres derived from  
 15 cenospheres having a mean size of 150 microns, 30% by volume of Scotchlite glass microspheres having a mean size of 30 microns, and 15% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

20 Water and the following additives were mixed with the powder so that the volume percentage of the liquid in the slurry was 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based  
 25 on polynaphthalene sulfonate at 0.07 gallons per bag of powder.

Slurry B: A mixture of powders was prepared. It comprised 55% by volume hollow spheres derived from cenospheres having a mean size of 150 microns, 25% by volume of Scotchlite glass microspheres having a mean size of 30 microns, and 20% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

Water and the following additives were mixed with the powder so that the volume percentage of the liquid in the slurry was 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based on polynaphthalene sulfonate at 0.07 gallons per bag of powder.

Slurry	A	B
Density	990 (8.25)	1056 (8.8)
Porosity	42%	42%
CS (24 h)	11.2 (1630)	21.4 (3100)
CS (48 h)	11.7 (1700)	22.1 (3200)

Densities are expressed in  $\text{kg/m}^3$  (and in pounds per gallon in parentheses). CS means compression strength after 24 hours and 48 hours for cement set at 60°C under a pressure of 6.9 MPa (1000 psi), expressed in MPa (and in pounds per square inch in parentheses).

Increasing the content of micro-cement and slag mixture gives rise to exceptional compression strength performance at 9 ppg.

#### EXAMPLE 4

Depending on the desired mechanical properties (flexibility, ability to withstand high pressures), various lightweight particles can be used so long as the PVF is optimized.

Slurry A: A mixture of powders was prepared. It comprised 55% by volume hollow spheres derived from cenospheres having a mean size of 150 microns, 30% by volume of hollow spheres derived from cenospheres having a mean size of 45 microns, and 15% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

Water and the following additives were mixed with the powder so that the volume percentage of the liquid in the slurry was 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based on polynaphthalene sulfonate at 0.07 gallons per bag of powder.

Slurry B: A mixture of powders was prepared. It comprised 55% by volume of particles of polypropylene having a means size of 300 microns, 30% by volume of Scotchlite glass microspheres having a mean size of 30 microns, and 15% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

Water and the following additives were mixed with the powder so that the volume percentage of the liquid in the slurry was 42%: a retarder based on purified lignosulfonates at 0.22% by weight of powder; a water retainer based on AMPS polymer at 0.2% by weight of powder; and a super-plasticizer based on polynaphthalene sulfonate at 0.05 gallons per bag of powder.

Slurry	A	B
Density	990 (8.25)	1068 (8.9)
Porosity	42%	42%
PV	93	116
Ty	20	9.3
CS (24 h)	18.3 (2640)	10.3 (1500) *
CS (48 h)	18.7 (2700)	22.1 (3200) *

Densities are expressed in  $\text{kg/m}^3$  (and in pounds per gallon in parentheses). Rheology is expressed by the flow threshold  $T_y$  in Pascals (and in pounds per 100 square feet in parentheses), and by plastic viscosity  $PV$  in  $\text{mPa}\cdot\text{s}$  or centipoises, using the Bingham  
5 fluid model. These parameters were determined at ambient temperature. CS means compression strength at 24 hours and at 48 hours from the cement setting at  $60^\circ\text{C}$  under 6.9 MPa (1000 psi), expressed in MPa (and in pounds per square inch in parentheses).

- 10 \* Compression strength at 24 hours for cement set at  $104^\circ\text{C}$  ( $220^\circ\text{F}$ ) under a pressure of 20.7 MPa (3000 psi), expressed in MPa and in psi in parentheses.

#### EXAMPLE 5

- 15 For low temperature applications, the mixture of micro-cement and slag can be substituted by pure micro-cement, or plaster can be added to replace the medium-sized particles.

We have compared a formulation of the invention with a foamed plaster formulation.

- 20 Slurry A: A mixture of powders was prepared. It comprised 42.7% by volume of hollow spheres derived from cenospheres having a mean size of 150 microns, 20% by volume of hollow spheres derived from cenospheres having a mean size of 45 microns, 27.3% by volume of gypsum, and 10% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

- 25 Water and the following additives were mixed with the powder so that the volume percentage of liquid in the slurry was 42%: retarder based on purified lignosulfonates at 0.05 gallons per bag of powder; a water retainer of the example at 0.04 gallons per bag of powder; and an antifoaming agent at 0.03 gallons per bag of powder.

30

Slurry B (reference): This slurry corresponds to the prior art. A mixture of powders was prepared. It comprised 40% by volume of class G cement and 60% by volume of plaster. Water and additives were mixed with the powder so that the density of the slurry was 1900 kg/m<sup>3</sup> (15.8 ppg).

To foam this slurry, entirely conventional wetting agents were added: D138 and F052.1 in a 1:1 ratio. The quantity added depends on foam quality. It was adjusted so as to obtain a slurry having a density of 1320 kg/m<sup>3</sup> (11 pounds per gallon).

Densities		1320 (11)	1218 (10.15)
Slurry A (of the invention)	Q		0
	PV		112
	Ty		6.7
	CS (at 12 hours for cement set at 4°C under 6.9 MPa)		2.41 (350)
	CS (at 24 hours for cement set at 25°C under 6.9 MPa)		14.8 (2150)
Slurry B (reference)	Q	30%	
	CS (at 24 hours for cement set at 18°C under atmospheric pressure)	2.96 (430)	
	CS (at 48 hours for cement set at 18°C under atmospheric pressure)	4.55 (660)	

Densities are expressed in kg/m<sup>3</sup> (and in pounds per gallon in parentheses). Rheology is expressed by the flow threshold Ty in Pascals (and in pounds per 100 square feet in parentheses), and by plastic viscosity PV in mPa.s or centipoises, using the Bingham fluid model.

These parameters were determined at ambient temperature. CS stands for compression strength under conditions stated in the table, expressed in MPa (and in pounds per square foot in parentheses).

- 5 It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

- 10 In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A cement slurry for cementing well, the slurry having a density between 0.9 g/cm<sup>3</sup> to 1.3 g/cm<sup>3</sup>, and being constituted by a solid fraction and a liquid fraction,  
5 having a porosity (volume ratio of liquid fraction over solid fraction) between 38% to 50%, said solid fraction comprising :
  - . 60% to 90% (by volume) of lightweight particles having a mean size between 20 microns(μm) to 350 μm;
  - . 10% to 30% (by volume) of micro-cement having a mean particle diameter  
10 between 0.5 μm to 5 μm;
  - . 0 to 20% (by volume) of Portland cement, having particles with a mean diameter between 20 μm to 50 μm; and
  - . 0 to 30% (by volume) of gypsum.
- 15 2. A cement slurry according to claim 1, in which the well is an oil well or gas well.
3. A cement slurry according to claim 1 or 2, having a porosity of less than 45%.
- 20 4. A cement slurry according to any preceding claim, in which the lightweight particles have a density of less than 2 g/cm<sup>3</sup>.
5. A cement slurry according to any one of claims 1 to 3, in which the lightweight particles have a density of less than 0.8 g/cm<sup>3</sup>.
- 25 6. A cement slurry according to claim 4 or 5, in which the lightweight particles are selected from hollow microspheres, synthetic materials, ceramic microspheres, or beads of plastics material.
- 30 7. A cement slurry according to claim 6 in which the microspheres are silico-aluminate microspheres or cenospheres.
8. A cement slurry according to claim 6 in which the synthetic materials are hollow glass beads or beads of sodium-calciumborosilicate glass.
- 35 9. A cement slurry according to claim 6 in which the ceramic microspheres are of the silica-alumina type.
- 40 10. A cement slurry according to claim 6 in which the beads of plastics material are polypropylene beads.

11. A cement slurry according to any preceding claim, in which the slurry has one or more additives of the following types: dispersants, antifreeze, water retainers, cement setting accelerators or retarders, or foam stabilizers.

5

12. A cement slurry according to any preceding claim, in which the solid fraction of the slurry is constituted by lightweight particles having a diameter between 100  $\mu\text{m}$  to 350  $\mu\text{m}$  and by particles of microcement, with the ratio of lightweight particles to microcement between 70: 30 to 85: 15.

10

13. A cement slurry according to any preceding claim, in which the solid fraction of the mixture is constituted by 50% to 60% (by volume) of first lightweight particles having a mean diameter between 100  $\mu\text{m}$  to 400  $\mu\text{m}$ , by 30% to 45% of second lightweight particles of mean diameter between 20  $\mu\text{m}$  to 40  $\mu\text{m}$ , and by 5% to 20% of micro-cement.

15

14. Use of the slurry according to any preceding claim in cementing oil, gas, or similar wells.

20

15. A cement slurry for cementing an oil well substantially as herein described with reference to the accompanying examples excluding results relating to slurry E in example 1 and reference slurry B in example 5.

25

16. Use of a cement slurry substantially as herein described with reference to the accompanying excluding results relating to slurry E in example 1 and reference slurry B in example 5.

Dated this 3rd day of March 2004

30

SOFITECH N.V.

By their Patent Attorneys

GRIFFITH HACK

Fellows Institute of Patent and

Trade Mark Attorneys of Australia

35