Title: CEMENTS CONTAINING HIGH-SILICA MINERALS FOR WELL CEMENTING

Abstract: A method of cementing high-temperature wells (e.g. above 110°C [230°F]) by pumping into the well a cement blend comprising Portland cement and a silica-rich mineral, the blend having a C/S molar ratio of less than about 2.0, preferably less than 1.6. This avoids the use of finely divided silica while preventing strength regression. The slurry can comprise a blend of Portland cement and pozzolanic materials (blast furnace slags, fly ash, etc.) such that the chemical composition (expressed in oxides) has a CaO/SiO₂ molar ratio below 1.7. A preferred composition is a mixture Portland cement and blast furnace slags with more than 60% of slags. The Blaine fineness of this material can be between 2,500 and 12,000 cm²/g and preferentially between 3,000 and 5,000 cm²/g.
CEMENTS CONTAINING HIGH-SILICA MINERALS FOR WELL CEMENTING

The present invention relates to the use of cement blends containing Portland cement and minerals having a high silica content for the cementing of wells such as oil, gas, water or geothermal wells, and in particular to cementing such wells at high temperatures.

Oil well cements are typically manufactured to comply with the American Petroleum Institute specification 10 which specifies chemical and physical parameters to which the cement must adhere. These parameters include compositional requirements and physical limits such as fineness. API Class G oil well cement is defined as a basic cement in which no additives are interground or blended during manufacture. As manufactured it is considered appropriate for use from surface to 8000 ft (2440m) depth, or can be used with chemical admixtures to cover a wider range of temperatures and depths.

The basic chemistry of oil well cements is similar to that of construction cements but hydration generally occurs at a slower rate. Standard conditions for hydration reactions in actual wells are non existent (conditions vary from well to well and even within a single well), therefore the behaviour of oil well cement products depend on the particular conditions encountered which affect the reaction.

Oil well cements are often used with the addition of admixtures to obtain the required slurry properties, depending on the well conditions i.e. temperature and pressure. These admixtures are used in combination and include, for example, retarders, antifoam agents, dispersants and fluid loss controllers.

Portland cement is essentially a calcium silicate material, the most abundant components being tricalcium silicate (C₃S) and dicalcium silicate (C₂S) which represent about 75-80% of cement (the following abbreviations are used unless otherwise indicated: C = CaO, A = Al₂O₃, S = SiO₂, H = H₂O). There is also a C₃A phase, the amount of which is critical for the chemical durability to sulphates and has also a significant impact on the rheological properties of cement slurries. Most oilwell
cements are commercially available as MSR (moderate sulphate resistant, 3% < C₃A < 8%) or HSR (high sulphate resistant, C₃A < 3%). Upon addition of water, the C₃S and C₂S phases hydrate to form a quasi-amorphous calcium silicate hydrate called "C-S-H gel," which is responsible for the strength and dimensional stability of the set cement at ordinary temperatures. In addition to C-S-H gel, a substantial amount of calcium hydroxide (CH) is liberated. C-S-H gel is an excellent binding material at well temperatures less than about 110°C (230°F). At higher temperature, C-S-H gel is subject to metamorphosis, which results in decreased compressive strength and increased permeability of the set cement. C-S-H gel converts to a phase called "alpha-dicalcium silicate hydrate (α-C₂SH)." α-C₂SH is highly crystalline and much more dense than C-S-H gel. As a result, a shrinkage occurs which is deleterious to the integrity of the set cement. This phenomenon is known as "strength retrogression."

The strength retrogression problem can be prevented by reducing the bulk lime-to-silica molar ratio (C/S molar ratio expressed as oxides) in the cement. The typical C/S molar ratio of Portland cement is around 3. The conversion of C-S-H gel into α-C₂SH at temperature above 110°C (230°F) can be prevented by the addition of 35% to 40% BWOC (By Weight Of Cement) of fine silica sand and/or silica flour, reducing the C/S molar ratio to about 1.0-1.2. At this level, a mineral known as 11 Å tobermorite (C₃S₆H₆) is formed; fortunately, high compressive strength and low permeability are preserved. As the curing temperature increases to about 170°C (338°F), 11 Å tobermorite normally converts to xonotlite (C₆S₆H) with minimal deterioration. Tobermorite sometimes persists to about 200°C (392°F) in Portland cement systems because of aluminium substitution in the lattice structure.

In some areas, oilwell cements are commercially available where 35-40% BWOC of quartz (silica) has been intergrated with Portland cement. However, in most cases the blend has to be made by cementing service companies. This operation is not very popular since it requires special equipments (at least two silos) and is time consuming. Moreover, fine silica is dangerous to manipulate (e.g. causing silicosis after prolonged exposure).
The present invention seeks to avoid the problems involved in the use of silica in oilwell cements.

In accordance with the present invention, there is provided a method of cementing wells, such as high-temperature wells (e.g. above 110°C [230°F]), by pumping into the well a cement blend comprising Portland cement and a silica-rich mineral, the blend having a C/S molar ratio of less than about 2.0.

Particularly preferred examples of the silica-rich minerals used in the invention are pozzolanic materials (blast furnace slags, fly ash, etc.). In such a case, it is preferred that the C/S ratio is less than 1.7. A preferred composition is a mixture Portland cement and blast furnace slags with more than 60% of slags. The Blaine fineness of this material can be between 2,500 and 12,000 cm²/g and preferentially between 3,000 and 5,000 cm²/g.

It is particularly preferred that the C/S ratio is less than 1.6.

The C/S molar ratio of the cement blend is decreased by adding silica-rich minerals, pozzolanic materials such as blast furnace slag and/or Class F (low content in CaO) flyash (pulverized fuel ash), that take part in the cement hydration reactions and thereby make a substantial contribution to the hydration product. The silica-rich mineral addition may be ground together with the cement clinker and gypsum, or mixed with Portland cement when the latter is used. Flyash and slag are waste materials produced in large quantities, and concretes (construction cements, cement/aggregate mixtures) made with them can have properties similar to those of ones made with pure Portland cements at lower cost per unit volume. Flyash is ash separated from the flue gas of a power station burning pulverized coal. Blast furnace slag is formed as a liquid at 1350-1550°C (2462-2822°F) in the manufacture of iron as a result of limestone reacting with materials rich in SiO₂ and Al₂O₃ associated with the ore or present in ash from the coke. If cooled sufficiently rapidly to below 800°C (1472 °F), it forms a glass which is a latent hydraulic cement.
Nowadays many blended cements are commercially available and can contain large proportions of flyash or slag, going up to over 80% by weight in the blend. Such cements are not normally used for oilwell cementing or the like. When large proportions of flyash or slag are present, the C/S molar ratio of blended cement can be less than 1.6, and such C/S molar ratios can be sufficiently low to prevent the formation of $\alpha$-C$_2$SH and calcium hydroxide when the cement is cured at temperature above 110°C (230°F). Thus, blended commercial cements can be suitable for high-temperature oilwell cementing if high compressive strength and low permeability can be achieved. Thus, the need for a blend of Portland cement and silica might be eliminated.

Oil well cementing compositions according to the present invention relates have a chemical composition significantly different from conventional oil well cement, and provide the following benefits:

- below 230°F (110°C), the amount of portlandite (Ca(OH)$_2$) that is formed during hydration is significantly reduced and the amount of C-S-H gel increased. This results in a denser matrix which is much less permeable and shows better resistance to brines.

- Above 230°F (110°C), the alpha dicalcium silicate phase which is detrimental for the mechanical properties and the permeability, is not formed, and by consequence the addition of silica is not needed (thus avoiding the need to blend cement and silica on-site and avoiding the need to handle fine silica materials).

- When combined with cenospheres, the material does not induce the hydration of these cenospheres due to the lack of portlandite. As a consequence, the porosity of the cement does not increase during hydration, so the permeability of the resulting set cement is lower and the chemical durability better.

- The cement material can also be used in a cementing composition having an engineered particle size distribution designs as fine particles for slurries with density below 10 ppg (pound per gallon) or as medium particles for slurries above 10 ppg.
- The amount of C₃A is typically very low (below 3%) in this material which makes it an inherently high sulphate resistant material.

Fly ash that is formed during the process of coal combustion in typical steam power plant generation contains a certain amount of fine spherical particles known as "cenospheres" (also called glass beads, hollow ceramic spheres or microspheres). Due to their unique combination of spherical shape, controlled sizing (after processing), relatively high strength in uniform compression, good thermal and acoustical insulating and dielectric properties, many high value applications can be made with these materials. Cenospheres have various applications which include lightweight mineral fillers in oil well cement slurries.

Cenospheres are hollow alumino-silicate vitreous spheres filled with air and/or other gases. Their shell thickness is about 5% of the diameter. Alumino-silicate glass predominates with negligible crystalline matter. However, a few spheres have significant crystal growth of mullite (Al₆Si₂O₁₃).

Cenospheres are relatively, chemically inert and offer a good resistance to solvent and acids, but in presence of calcium and at high pH (>13), silicoaluminates react with calcium to produce a cementitious material composed of calcium silicate hydrate (called "C-S-H gel") containing aluminium ions.

When cenospheres are combined with Portland cement to provide light weight slurries, these chemical criteria are met. As the Portland cement starts to set, there is a significant increase of pH due to the release of alkalis into the liquid phase, and calcium hydroxide is always available. At that point, cenospheres start to hydrate. Due to the small thickness of the shell, the void inside the particle becomes rapidly part of the porosity of the set cement matrix (in cementing terms, "porosity" is used to express the liquid or non-solid part of the blend, consequently hollow particles are not considered as porous as the enclosed space normally takes no part in the formation of the set cement and the particle appears to the system merely as a low density solid). However, the cementing composition of the present invention avoids this problem since there is relatively little calcium hydroxide present with which the cenospheres can react. Because the reactivity of the cenospheres can be controlled, it is possible to
produce very low density slurries using a combination of cenospheres and foam with a reduced risk of excessive permeability being produced in the resulting cement. Compositions according to the invention include blends of cement, silica-containing minerals (e.g. slags) and hollow particulate materials (e.g. cenospheres). Foamed compositions can be created by injecting gas into a slurry of this composition.

The present invention will now be described by way of examples and with reference to the accompanying drawings, in which:

Figure 1 shows photomicrographs of a cement slag blend (CLK cement) cured for four weeks at 150\°C (302\°F);
Figure 2 shows photomicrographs of a Class G cement cured for four weeks at 150\°C (302\°F);
Figure 3 shows photomicrographs of a Class G cement/35% BWOC silica flour blend cured for four weeks at 150\°C (302\°F);
Figure 4 shows X-ray diffraction spectrum of a set Portland cement with cenospheres;
Figure 5 shows X-ray diffraction spectrum of cenospheres; and
Figure 6 shows X-ray diffraction spectrum of a cement composition according to the invention with cenospheres.

The hydrothermal behaviour of a commercial blended cement (supplied by Origny Company) is studied at 150\°C (302\°F), and compared to two other cement systems: 1) pure Class G Portland cement, 2) Class G Portland cement stabilized with 35% BWOC silica flour. This commercial cement, which is commonly used in construction industry, is composed of about 20% Portland cement and about 82% blastfurnace slag (of CLK type in French cement nomenclature). The oxide composition and C/S molar ratio of the three cement systems are given in Table 1. The composition of cement slurries is given in Table 2.
### Table 1: Oxide Composition and C/S Molar Ratio of Cement Systems

<table>
<thead>
<tr>
<th>Oxide Composition:</th>
<th>CLK cement</th>
<th>Class G* cement</th>
<th>Class G cement + 35% BWOC Silica Flour</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>44.32</td>
<td>63.12</td>
<td>46.76</td>
</tr>
<tr>
<td>SiO₂</td>
<td>31.41</td>
<td>22.55</td>
<td>42.63</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.72</td>
<td>3.90</td>
<td>2.89</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.37</td>
<td>4.71</td>
<td>3.49</td>
</tr>
<tr>
<td>MgO</td>
<td>6.39</td>
<td>0.75</td>
<td>0.56</td>
</tr>
<tr>
<td>C/S Molar Ratio</td>
<td>1.51</td>
<td>3.00</td>
<td>1.17</td>
</tr>
</tbody>
</table>

* API (American Petroleum Institute) Classification for oilwell cements. Class G cement is commonly used at high temperature.

### Table 2: Composition of Cement slurries

<table>
<thead>
<tr>
<th></th>
<th>CLK cement</th>
<th>Class G cement</th>
<th>Class G cement + 35% BWOC Silica Flour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anti-foam agent (L/tonne of cement)</td>
<td>2.7</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Retarder (% BWOC)</td>
<td>-</td>
<td>0.3</td>
<td>0.25</td>
</tr>
<tr>
<td>Retarder/Dispersant – solid (% BWOC)</td>
<td>-</td>
<td>0.3</td>
<td>0.25</td>
</tr>
<tr>
<td>Retarder/Dispersant – liquid (L/tonne of cement)</td>
<td>6.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Water (L/tonne of cement)</td>
<td>411</td>
<td>424</td>
<td>538</td>
</tr>
<tr>
<td>Slurry Density (kg/L)</td>
<td>1.87</td>
<td>1.92</td>
<td>1.92</td>
</tr>
<tr>
<td>Slurry Porosity (%)</td>
<td>55.4</td>
<td>56.9</td>
<td>54.6</td>
</tr>
</tbody>
</table>
600 mL of cement slurry is mixed according to the API procedure in a Waring blender mixer rotating at 12,000 RPM for 35 seconds. The slurry is then introduced in a UCA (Ultrasonic Cement Analyzer) cell to follow the development of compressive strength at 150°C (302°F) under a 3000 psi (20.7 MPa) confining pressure. The cement is heated from ambient temperature to 150°C (302°F) at 2.78°C/min (5°F/min) to avoid a thermal shock.

After two or three days of curing at 150°C (302°F) the compressive strength of the three cement systems stabilizes at 4700 psi (32.4 MPa) for the CLK cement, 2500 psi (17.2 MPa) for the Class G cement without addition of silica flour, and at 5500 psi (37.9 MPa) for the Class G cement stabilized with 35% BWOC silica flour. No further evolution is noted after 4 weeks and the experiments stopped.

The compressive strength of CLK cement is quite comparable to that obtained with the Class G cement stabilized with silica, and is sufficiently high to protect the casing against mechanical stresses which can be encountered in the well. The lower compressive strength of Class G cement without addition of silica is due to “strength retrogression” phenomenon which occurs during the first day of curing.

After four weeks curing at 150°C (302°F), set cement samples are crushed and dried with acetone and ethyl ether to remove the water which is not chemically bound in cement hydrates. Hydration products are analysed by thermogravimetric analysis (TGA) and X-rays diffraction (XRD). XRD allows to detect crystalline compounds, whereas TGA enables to highlight the presence of α-C₂SH and calcium hydroxide (CH) thanks to their characteristic water weight loss occurring in 450-500°C (842-932°F) temperature range.

The only crystalline hydrate detected by XRD in hydrated CLK cement is 11 Å aluminium-substituted tobermorite (up to 10% of silicon can be substituted by aluminium in its lattice structure), while α-C₂SH and calcium hydroxide is not detected by both techniques. The presence of poorly crystallized C-S-H gel is also likely.
As expected the hydrated Class G cement is mainly composed of $\alpha$-C$_2$SH and calcium hydroxide. Tobermorite and C-S-H gel is not detected. The presence of large amounts of $\alpha$-C$_2$SH and calcium hydroxide can explain the low compressive strength value.

The hydrated Class G cement stabilized with 35% BWOC silica flour reveals the presence of small quantities of $\alpha$-C$_2$SH and silica that has not reacted with the cement. Nevertheless, 11 Å tobermorite is the major hydration product.

Set cements cured for four weeks at 150°C (302°F) are observed by Scanning Electron Microscopy (SEM).

Figure 1 shows that the matrix of CLK cement is very compact, probably resulting in low permeability value. In small holes hydration products have some space to develop, they are poorly crystallized and look like those obtained at temperature below 110°C (230°F) where the C-S-H gel is predominant. Crystals of $\alpha$-C$_2$SH and calcium hydroxide were not observed; this is in agreement with the results obtained by TGA and XRD.

Figure 2 shows that the matrix of Class G cement is very porous with the presence of big holes between crystallized hydrates. These crystals mainly appear as plates which are characteristic of $\alpha$-C$_2$SH. Some smaller hexagonal crystals of calcium hydroxide could also be distinguished. It is most likely that the permeability of this cement matrix is quite high.

The effect of silica added to Class G cement can clearly be seen in Figure 3. The matrix is much more compact and, therefore, has probably a low permeability. The morphology of hydrates is representative of that described in the literature for well-crystallized 11 Å tobermorite.

The water permeability of CLK cement cured for five days at 150°C (302°F) is measured to be less than 6 μD which corresponds to the detection limit of the equipment used. Actually, the true permeability is likely much lower than this value.
It is generally recognized that the water permeability of oilwell cements should be no more than 100 μD to prevent interzonal communication.

The benefits of the present invention can also be demonstrated in the following experiments:

Experiment I
This experiment demonstrates the chemical reactivity of cenospheres with conventional Portland cement:
A cement slurry was prepared by mixing:
- a blend of Portland cement Class G, and cenospheres (specific gravity of 0.75, average particle size 130 microns) present in an amount of 35% by weight of cement;
- a mixing fluid composed of 10.1 gallons per sack (gps) of cement of water, 0.04 gps of liquid antifoam and 0.4 % by weight of blend (BWOB) of an antisettling agent.
The mixed slurry has a specific gravity of 1.32 (11 ppg).

This cement slurry is then cured in a curing chamber under 3000 psi at 302°F (150°C) for 5 weeks. After, cooling, the set cement is dried with acetone and ethyl ether and then analysed:

1) X ray diffraction characterization
The X-ray diffraction spectrum of the sample is shown in Figure 4 and can be compared with that of cenospheres as shown in Figure 5. No peaks specific of the mullite phase (arising only from cenospheres) can be observed in this sample as can be seen in the spectrum (Figure 4) indicating that the cenospheres have reacted during the curing process and have broken down.

2) Scanning electron microscopy (SEM)
SEM analysis of the sample shows that the integrity of the shell of the cenospheres is not maintained. Most of the spheres are opened.
Experiment II

The chemical composition of the cementitious material according to the invention (20% Portland cement/80% slags in this example), there is no calcium hydroxide available to promote the reactivity of the silicoaluminates in the cenospheres. This can be shown by doing the same experiment as in I above but replacing the Portland Class G cement by the cementitious material according to the invention, exactly in the same amount:

1) X-ray diffraction characterization

The peaks specific to the mullite phase (indicating the presence of complete cenospheres) can be easily observed in this sample as can be seen in the spectrum (Figure 6) when compared to the spectrum of the cenospheres (Figure 5).

2) Scanning electron microscopy

By SEM one can observe that the integrity of the shell of the hollow spheres is maintained.

Contrary to Portland cement, when combined with cenospheres, the cementitious material according to the invention does not induce any chemical modification of these cenospheres. As a consequence, the voids which compose the core of the cenospheres are not part of the porosity of the set material, that decreases significantly the permeability and increase the chemical durability when compared to normal Portland cement.

Cenospheres are known to have a higher chemical resistance to brines but also to acids compared to cementitious hydrates. By avoiding their hydration when combined with a cementitious material, the chemical durability of the set cement matrix is improved.

Experiment III

The following slurries are prepared:
a. Class G cement was mixed with fresh water, 0.03 gps of antifoam, and 0.04 gps of dispersant so that the density of the slurry is 16 ppg (cement slurry porosity of 59%);
b. Class G cement is blended with cenospheres (specific gravity of 0.75, average particle size 130 microns) respectively in 40%/60% volume ratio. This blend is then mixed with fresh water, 0.03 gps of antifoam, and 0.4% by weight of blend (BWOB) of anti-settling agent so that the density of the slurry is 11.4 ppg (cement slurry porosity of 50%).

These two cement slurries are cured under 3000 psi at 185°F (85°C) for 72 hours.

The cement cubes are weighted, then immersed into a 12% HCl solution. After 24 hours, the weight loss of the cubes made from the blend Class G/cenospheres was 31% greater than the neat Class G.

This experiment is repeated with the same slurry designs but with a cementitious material composed of 20% Portland cement and 80% slag (cement X):

c. Cement X is mixed with fresh water, 0.03 gps of antifoam, and 0.05 gps of dispersant so that the density of the slurry is 15.2 ppg (porosity 59%).

d. Cement X is blended with cenospheres (specific gravity 0.75, average particle size 130 microns) respectively in a 40%/60% volume ratio. This blend is then mixed with fresh water, 0.03 gps of antifoam, and 0.4% BWOB of anti-settling agent so that the density of the slurry is 11 ppg (cement slurry porosity of 50%).

These two cement slurries are cured under 3000 psi at 185°F (85°C) for 72 hours.

The cubes are weighted, then immersed into a 12% HCl solution. After 24 hours, the weight loss of the cubes made from the Cement X/cenospheres is 23% less than the neat Cement X.

This experiment demonstrates that maintaining the integrity of cenospheres can improve significantly the chemical durability of the set cement.
By using the appropriate cementitious material, one can control the chemical reactivity of cenospheres. Depending on the final properties of the set cement which are required, this reactivity can be enhanced or prevented (chemical resistance).

Preventing the chemical reactivity of cenospheres has a tremendous impact on the permeability. Foaming cement slurries with nitrogen to obtain light weight cement is commonly used. However, it is also well known that foaming is detrimental for the final permeability of the set material. Therefore, a foamed cement slurry containing cenospheres and Portland cement will give a final material with a high permeability (> 0.1 mDarcy).

The following example will show how the permeability can be significantly reduced when in such systems Portland cement is replaced by a cementitious material as defined by the invention.

Experiment IV

The following cement slurries are prepared:

a) Cement X is blended with cenospheres (specific gravity of 0.75, average particle size 130 microns) respectively in a 40%/60% volume ratio. This blend is then mixed with fresh water, and 0.08 gps of surfactants are added and the slurry is mixed in a closed warring blender so that the foam quality is 30% (that is the volume of gas represents 30% of the total volume of cement slurry). The final density of the slurry is 7.6 ppg.

b) Class G cement is blended with cenospheres (specific gravity of 0.75, average particle size 130 microns) respectively in a 40%/60% volume ratio. This blend is then mixed with fresh water, and 0.08 gps of surfactants are added and the slurry is mixed in a closed warring blender so that the foam quality is 30%. The final density of the slurry is 7.9 ppg.

These two cement slurries are cured at 185°F (85°C) in a close cell (to avoid gas expansion) for 48 hours. The water permeability of the set materials is then measured:

- Formulation with Class G cement: 10 mDarcy
- Formulation with Cement X: < 0.1 mDarcy

There is at least 2 orders of magnitude in the permeability which is a significant improvement. The cementitious material related to the invention is therefore particularly efficient to foam cement slurries containing cenospheres, allowing to reach very low densities but still keeping an acceptable permeability (< 0.1 mDarcy).

Cement compositions according to the invention can form part of an engineered particle size distribution system such as that described in EP 621247. Engineered particle size distribution is a concept that optimises the Packing Volume Fraction (PVF) of a blend of solid particles which allows the preparation of slurries with a high content of solid (up to 62% of the total volume of slurry) with a low rheology. This optimised PVF is achieved by choosing an appropriate combination of particles in term of particle size and ratio. As long as these size criteria are met, the different particles may have any specific gravity, allowing the preparation of slurries from 6 ppg to 24 ppg. The cementitious material according to the invention can be used instead of Portland cement in such slurries and preferentially when cenospheres are one of the other particles. This will reduce the total porosity of the set cement as it does not induce the hydration of the cenospheres.

Experiment V

A blend of a cementitious material (20% Portland/80% slags, the mixture having an average particle size of 12 microns) with Cenospheres having a particle size distribution (average particle size of 130 microns) such that the blend has a PVF around 0.8 and a specific gravity of 1.17, is prepared. A mixed fluid containing 6.71 gpbs (gallon per 100 pounds of blend) of water, 0.07 gpbs of a liquid antifoam, 0.6 gpbs of a fluid loss control agent, 0.03 gpbs of retarder and 0.01 gpbs of a dispersant is prepared. When the blend is mixed with the mixed fluid, the cement slurry density is 1.1 (9.2 ppg).

The system properties are as follows:
<table>
<thead>
<tr>
<th>Slurry Density</th>
<th>1.10 (9.2 ppg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry Porosity</td>
<td>42%</td>
</tr>
<tr>
<td>Plastic Viscosity (mPa.s)</td>
<td>111</td>
</tr>
<tr>
<td>Yield Stress (Pa)</td>
<td>1.4</td>
</tr>
<tr>
<td>Thickening time</td>
<td>3 hours</td>
</tr>
<tr>
<td>Compressive Strength at 24 hours</td>
<td>13.8 MPa (2000 psi)</td>
</tr>
</tbody>
</table>

The rheological values (Bingham model) are obtained after conditioning for 20 minutes the cement slurry at 130°F (54°C).

The final compressive strength is measured after a cure of 24 hours at 158°F (70°C).

The water permeability measurement is below the detection limit of the test equipment used (5 micro Darcy).

It will be appreciated that different cement compositions from those described above may be prepared without departing from the concept of the present invention.
CLAIMS

1. A method of cementing a well, comprising pumping into the well an aqueous cement slurry including a mixture of Portland cement and a silica-rich mineral, the mixture having a C/S molar ratio of less than about 2.0.

2. A method as claimed in claim 1, wherein the well has a temperature above 110°C (230°F).

3. A method as claimed in claim 1 or 2, wherein the cement blend is substantially free of finely divided silica, silica flour, silica sand or silica fume.

4. A method as claimed in claim 1, 2 or 3, wherein the cementing composition develops high compressive strength and low permeability when cured at temperature above 110°C (230°F).

5. A method as claimed in any preceding claim, wherein the Portland cement comprises ordinary Portland cement (OPC); Class A, B, C, G or H of API classification, Type I to V of ASTM classification or pozzolan cement.

6. A method as claimed in any preceding claim, wherein the silica-rich mineral comprises blastfurnace slag, flyash, natural pozzolans or metakaolin.

7. A method as claimed in claim 6, wherein the flyash is of Class F (low content in lime, CaO < 10%).

8. A method as claimed in any preceding claim, wherein the silica-rich mineral is present in an amount in the range of from about 40% to 100% of the mixture.

9. A method as claimed in claim 8, wherein the silica-rich mineral is present in an amount in the range of from 60% to 85% of the mixture.
A method as claimed in any preceding claim, wherein the slurry comprises a blend of Portland cement and pozzolanic material such that the chemical composition has a CaO/SiO$_2$ molar ratio below 1.7.

A method as claimed in claim 10, wherein the pozzolanic materials comprise blast furnace slag, and fly ash.

A method as claimed in claim 11, wherein the blend includes more than 60% of blast-furnace slag as the pozzolanic material.

A method as claimed in claim 12, wherein the blend comprises approximately 20% Portland cement and approximately 80% slag.

A method as claimed in any of claims 10 - 13, wherein the blend has a Blaine fineness of between 2,500 and 12,000 cm$^2$/g

A composition as claimed in claim 14, wherein the mixture has a Blaine fineness of between 3,000 and 5,000 cm$^2$/g.

A method as claimed in any preceding claim, further comprising a hollow particulate material.

A method as claimed in claim 16, wherein the hollow particulate material comprises cenospheres, glass micro-spheres, or ceramic spheres.

A method as claimed in any preceding claim, wherein the slurry further comprises anti-foam agents, dispersants, fluid-loss control additives, and/or retarders.

A method as claimed in any preceding claim, wherein the slurry further comprises a dispersed gas phase so as to form a foamed cement.

A method as claimed in any preceding claim, wherein the C/S molar ratio of slurry is less than 1.6.
Sillimanite (AS)
Mullite (A₂S₃)
FIGURE 6

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Sillimanite (AS)

Mullite (A_3S_2)

---

2-Theta - Scale
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C04B28/04
//((C04B28/04,18:08),(C04B28/04,18:14))

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C04B

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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X Further documents are listed in the continuation of box C.
X Patent family members are listed in annex.

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  *K* document member of the same patent family

Date of the actual completion of the international search
2 September 2003

Date of mailing of the international search report
09/09/2003

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk
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Authorized officer
Theodoridou, E.
# INTERNATIONAL SEARCH REPORT

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