



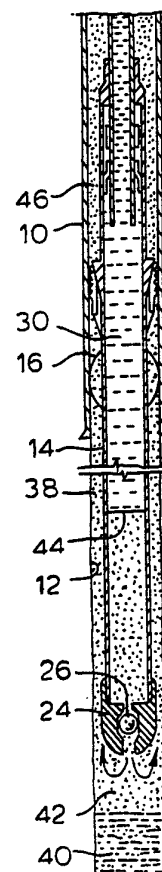
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(54) Title: METHOD FOR DRILLING AND CEMENTING A WELL

(57) Abstract

A borehole is drilled utilizing a conventional drilling fluid or a drilling fluid such as one containing a cementitious component selected from blast furnace slag, a metal oxide component of an ionomer or a metal oxide component of a phosphate salt. A compatible cementitious slurry containing blast furnace slag and an activator system is then introduced into the borehole and displaced up into an annulus by direct contact with a displacement fluid. Generally, in the case of the slag-containing drilling fluid the cementitious slurry is prepared by adding additional blast furnace slag and an activator such as a sodium hydroxide/sodium carbonate mixture to the used drilling fluid. Similarly, in the case of the ionomers or phosphates, additional metal oxide component and the reactive second component can be added to the used drilling fluid to produce the cementitious slurry.



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METHOD FOR DRILLING AND CEMENTING A WELL

This invention relates to drilling and cementing a well.

The rotary drilling of a borehole is accomplished using a rotary drilling assembly comprising a by rotating a drill bit attached to the lower end of a drill string. Weight is applied to the drill bit while rotating to create a borehole into the earth. The drill string is hollow and pipe sections are added to the drill string to increase its length as the borehole is deepened. In rotary drilling the drill bit can be rotated by rotating the drill string and/or by driving a downhole motor arranged at the lower end of the drill string.

This rotary drilling process creates significant amounts of friction which produces heat along with fragments of the strata being penetrated. The fragments of the strata must be removed from the borehole and the drill bit must be cooled to extend its useful life. Both of these necessities are accomplished by the circulation of a fluid down through the drill string and up to the surface between the drill string and the wall of the borehole.

Once the borehole has been drilled to the desired depth, it may be desirable to isolate the separate areas, zones or formations traversed by the borehole. For extraction of fluids from formations, a conduit (casing) must be inserted into the borehole extending from the surface downward, and liners may be hung inside the casing.

At this point it becomes necessary to fill the annulus between the casing and the borehole wall or between the liner and casing with a material which will seal the annulus and provide structural support for the casing or liner. This is commonly referred to as primary cementing.

Generally, the borehole is filled with drilling fluid, also referred to as drilling mud, which drilling mud has to be removed to fill the annulus between the casing and the borehole wall with

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cement. Therein lies a problem that has created primary cementing difficulties throughout the history of cementing. Conventional Portland cement and conventional drilling fluids are incompatible. Thus, as the cement is forced down the casing or liner and up into the annulus, it mixes with drilling fluid and the area around the end of the casing or liner being cemented as well as varying lengths of the annulus end up being filled with a mixture which does not set up into a strong cement.

It is generally necessary after setting each casing or liner to test the integrity thereof by means of a pressure test. However, if the area at the bottom end thereof is not sealed off, pressure testing fails. Hence, the industry has developed a complex system to circumvent this problem. A device generally known as a landing collar is attached to the bottom of the casing or liner being cemented. The casing or liner has an annular shoulder projecting inwardly. The cementitious slurry is introduced into the casing followed by a rubber wiper plug. Displacement fluid then pushes the wiper plug downward, thus displacing the cementitious slurry out of the casing and into an area at the bottom thereof where it changes direction and flows upwardly into the annulus. When the wiper plug reaches the area of the landing collar, it is stopped by the inwardly projecting shoulder and forms a seal so as to allow pressure testing, although a good seal is not always obtained. These problems are magnified with large diameter casings and liners.

Slag, broadly, as a cementitious material is shown in USA patent specification No. 3 557 876.

Cementing of the annulus between an oil well casing and the surrounding borehole has been practised for over 90 years. Long ago, it was recognized that it would be advantageous to solidify drilling fluid in the annulus so as to reduce the cost of the cementing of the casings. Over the decades, various attempts have been made along this line as evidenced by the disclosures in USA patent specifications No. 2 649 160 No. 3 887 009. However, such techniques, while presumably operable, have failed to achieve

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commercialization even after the passage of many years. Another attempt in this direction is described in USA patent specification No. 3 499 491, wherein Portland cement is used in an aqueous drilling fluid to produce a mud concrete. Portland cement, however, is very sensitive to the water/solids ratio. Even under ideal conditions, only small increases in the amount of solids results in a very viscous mass. On the other hand, only a slight decrease in the amount of solids results in a composition which sets up to give a very weak structure. These problems are amplified when attempting to use Portland cement in a drilling fluid. Thus, while this technique has been used commercially, it has serious drawbacks.

It is an object of this invention to cement a casing or liner without the necessity for a wiper plug or a float collar.

It is a further object of this invention to achieve a good seal in the annulus, thus sealing the casing and the surrounding borehole or pipe and, in cases where there is a rat hole, a good seal at the bottom end of a casing or liner being cemented.

It is a further object of this invention to avoid the problems of incompatibility between drilling fluid and cement at their interface during primary cementing.

It is yet a further object of this invention to economically seal large diameter casings and liners.

To this end the method for drilling and cementing a well according to the present invention comprises:

drilling a borehole utilizing a drilling fluid, thus producing a used drilling fluid;

combining ingredients comprising water, blast furnace slag and an activator to produce a cementitious slurry;

disposing a pipe in the borehole;

passing the cementitious slurry down the pipe; and

displacing the cementitious slurry up into an annulus surrounding the pipe through direct contact by a displacement fluid.

It has been discovered that by utilizing a cementitious slurry containing blast furnace slag and an activator cementing can be

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carried out without the necessity of using a wiper plug and float collar, i.e., by means of direct contact between the displacement fluid and the cementitious slurry.

5 In this description the term 'cementitious material' means either the hydraulic material, blast furnace slag, which, on contact with water and/or activators, hardens or sets into a solidified composition or a component which, on contact with a reactive second component, sets or hardens into a solidified composition. Thus, broadly, it can be viewed as a material which
10 can chemically combine to form a cement.

A slurry of this cementitious material and the component or components which cause it to harden is referred to herein as a "cementitious slurry".

The term 'universal fluid' is used herein to designate those
15 compositions containing cementitious material, which compositions are suitable for use as a drilling fluid, and which compositions thereafter, for the purpose of practising this invention, have additional cementitious material and/or activators such as accelerators (or reactive second components) added to give a
20 cementitious slurry.

By 'direct contact' between the displacement fluid and the cementitious slurry is meant that the displacement fluid directly contacts the upper surface of the column of cementitious slurry as opposed to having a wiper plug disposed between the cementitious
25 slurry and the displacement fluid. This also allows the operation to be carried out without a float collar to stop the wiper plug.

The term 'hydraulic material' means a material which, on contact with water and/or activators, sets to a hard material.

The term 'pipe' means either a casing or a liner.

30 The term 'primary cementing' refers to any cementing operation wherein a cementitious slurry is passed down a pipe and up into an annulus surrounding the pipe and a borehole or prior casing and thus encompasses both the cementing of casings wherein the annulus is between the casing and the borehole wall and the cementing of
35 liners where the annulus is between the liner and the casing.

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By 'activator system' is meant either the activators as in the case of blast furnace slag or the reactive second component of the proton accepting metal compounds. The reactive second component is either a polymer as described in detail hereinafter or a phosphorus acid as described in detail hereinafter.

The present invention further comprises a method for drilling and cementing a well, comprising:

combining blast furnace slag having a particle size between 2 000 and 15 000 cm^2/g with an aqueous drilling fluid, the blast furnace slag being present in an amount between 2.8 and 280 kg/m^3 of the drilling fluid plus blast furnace slag;

utilizing the drilling fluid in a well drilling operation to form a borehole to produce a used drilling fluid;

combining additional blast furnace slag and an activator with the used drilling fluid to produce a cementitious slurry;

disposing a pipe in the borehole;

passing the cementitious slurry down the pipe; and

displacing the cementitious slurry up into an annulus surrounding the pipe by direct contact with a displacement fluid.

The present invention comprises a method for drilling and cementing a well, comprising:

combining constituents comprising water and a metal compound proton accepting component to produce a drilling fluid;

utilizing the drilling fluid in a well drilling operation to form a borehole, thus producing a used drilling fluid and laying down a filter cake;

contacting a reactive second component with the filter cake;

disposing a pipe in the borehole after the filter cake is laid down;

passing a cementitious slurry down the pipe; and

displacing the cementitious slurry up into an annulus surrounding the pipe by direct contact with a displacement fluid.

The invention will now be described in more detail with reference to the the drawings in which drawings like reference numerals denote like parts in the various views, wherein

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Figure 1 is a cross sectional representation of a borehole with a liner being cemented in accordance with the prior art; and

Figure 2 is a cross sectional view of a similar borehole with a liner being cemented in accordance with the invention.

5 Referring now to Figure 1, there is shown a conventional cementing operation wherein a borehole has been drilled in a subterranean formation not according to the invention. A casing 10 is shown in an upper portion of the borehole and a further extension of the borehole as defined by borehole wall 12 is depicted. A liner pipe 14 is disposed in the borehole, which liner pipe 14 has to be cemented in place. Centralizers 16 center the liner pipe. Disposed at the bottom of the liner pipe is a landing collar 18 having an annular shoulder 20. Disposed within the liner pipe is wiper plug 22. A float shoe 24 having valve 26 is affixed to a lower portion of the landing collar. The borehole from the bottom thereof up to just below the float shoe is filled with the drilling fluid from the drilling operation, the drilling fluid being depicted by reference numeral 28. This part of the borehole is called the rat hole and is generally present although the float shoe can rest on the bottom of a borehole.

Figure 1 represents the prior art and shows the stage of the cementing operation wherein displacement fluid 30 has pushed wiper plug 22 down liner pipe 14 until it rests against shoulder 20 of landing collar 18, thus forming a seal. The cementitious slurry 32 has been forced down through valve 26 and out the bottom of the float shoe as indicated by the arrows 34. In doing this, the cementitious slurry 32 mixes with drilling fluid 28 to form an incompatible mixture 36 just below the float shoe and up the annulus between the float shoe and the borehole wall. Although not shown, this weak cement/mud mixture extends to varying degrees up the annulus between the casing 10 and the liner pipe 14, essentially all the way to the top of the annular cement column. Thus, the borehole is not well sealed. Hence the need for the seal between the wiper plug 22 and annular shoulder 20 of landing collar 18. The Figure shows the operation just as the cementitious slurry

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has been displaced into the annulus. As it is setting, the drilling fluid migrates up the inside of the float shoe and landing collar giving a weak cement or even causing the cementitious slurry not to set in a reasonable time.

5 Figure 2 shows the cementitious slurry displacement in accordance with the invention. Because a cementitious slurry 38 is used which is compatible with drilling fluid 40, the region 42 at the bottom of the float shoe and up the annulus is a compatible mixture of cementitious slurry and drilling fluid which will set to
10 a hard cement. As can be seen there is direct contact at interface 44 between the displacement fluid 30 and the compatible cementitious slurry 38.

 While this has been described in connection with the cementing of a liner wherein the cementitious slurry is forced into the
15 annular space 46 between the liner and the casing, it is equally applicable to cementing a casing wherein the cementitious slurry is forced up an annulus between the casing and the borehole wall.

 The term 'drilling fluid' as used herein means water or oil based fluids which contain water and at least one other additive
20 such as viscosifiers, thinners, dissolved salts, solids from the drilled formations, solid weighting agents to increase the fluid density, formation stabilizers to inhibit deleterious interaction between the drilling fluid and geologic formations, and additives to improve the lubricity of the drilling fluid.

25 Drilling can be carried out using a conventional drilling fluid or by utilizing a universal fluid as described herein.

 Generally, in the universal fluid embodiment, the starting material to which the cementitious material is added to give the universal drilling fluid used in this invention is a conventional
30 drilling fluid. The term 'water-based drilling fluid' is intended to encompass both fresh water drilling fluids, salt water-containing drilling fluids, whether made from seawater or brine, and other drilling fluids having water as the continuous phase including oil-in-water emulsions.

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It is sometimes desired that the water-based drilling fluids use water-containing dissolved salts, particularly sodium chloride. In these instances, 0.1 to 26 wt%, preferably 3 to 10 wt% sodium chloride may be used. One suitable source is to use seawater or a
5 brine solution simulating seawater. Particularly in the embodiment using slag, the strength of the resulting cement is actually enhanced which is contrary to what would be expected in view of the intolerance of Portland cement to brine. Various salts, preferably organic salts, are suitable for use in the drilling fluid used in
10 this invention in addition to, or instead of NaCl, including, but not limited to, NaBr, KCl, CaCl_2 , NaNO_3 , $\text{NaC}_2\text{H}_3\text{O}_2$, $\text{KC}_2\text{H}_3\text{O}_2$, NaCHO_2 and KCHO_2 among which sodium chloride is preferred, as noted above. These salts can be used, if desired, up to the saturation point under the conditions employed.

15 The term 'oil-based fluids' is meant to cover fluids having oil as the continuous phase, including low water content oil-base drilling fluid and invert oil-emulsion drilling fluid.

A typical drilling fluid formulation to which cementitious material may be added to form a universal drilling fluid is as
20 follows: 10-20 wt% salt, 23-28 kg/m^3 bentonite, 11-17 kg/m^3 carboxymethyl starch (fluid loss preventor), sold under the trade name "BIOLOSE" by Milpark Drilling Fluids, 1-3 kg/m^3 partially hydrolyzed polyacrylamide (PHPA) which is a shale stabilizer, sold under the trade name "NEWDRIL" by Milpark Drilling Fluids, 3-4
25 kg/m^3 CMC sold under the trade name "MILPAC" by Milpark Drilling Fluids, 85-200 kg/m^3 drill solids, and 0-715 kg/m^3 barite.

Thus, the universal fluid makes possible a method for drilling and cementing a well comprising preparing a universal fluid by mixing a drilling fluid and a cementitious material; drilling a
30 borehole with the universal fluid and laying down a settable filter cake on the wall of the borehole during drilling of the well; adding additional cementitious material and/or accelerators (or reactive second components) and introducing the thus-formed cementitious slurry into the borehole and into an annulus
35 surrounding a pipe in accordance with the direct displacement

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method of this invention where it hardens and sets up forming a good bond with the filter cake which filter cake, by itself, actually hardens with time because of the presence of cementitious material therein. This hardening is facilitated by any
5 accelerators which may be present in the cementitious slurry and which migrate by diffusion and/or filtration into the filter cake.

The cementitious material is one selected from the group consisting of blast furnace slag, a metal oxide component used to produce an ionomer and a metal oxide component used to produce a
10 phosphorus salt. By 'blast furnace slag' is meant the hydraulic refuse from the melting of metals or reduction of ores in a furnace as disclosed in USA patent specification No. 5 058 679, the disclosure of which is incorporated herein by reference. By 'phosphorus salt' is meant a phosphonate, a phosphate or a
15 polyphosphate as is described in detail hereinafter.

The preferred blast furnace slag used in this invention is a high glass content slag produced by quickly quenching a molten stream of slag at a temperature of between 1400 °C and 1600 °C through intimate contact with large volumes of water. Quenching
20 converts the stream into a material in a glassy state having hydraulic properties. At this stage it is generally a granular material that can be easily ground to the desired degree of fineness. Silicon dioxides, aluminium oxides, iron oxides, calcium oxide, magnesium oxide, sodium oxide, potassium oxide, and sulphur
25 are some of the chemical components in slags. Preferably, the blast furnace slag used in this invention has a particle size such that it exhibits a specific surface area between 2 000 cm²/g and 15 000 cm²/g and more preferably, between 3 000 cm²/g and 15 000 cm²/g, even more preferably, between 4 000 cm²/g and 9 000 cm²/g, most
30 preferably between 4 000 cm²/g and 8 500 cm²/g. In each instance the specific surface area or surface area is the Blaine specific surface area. An available blast furnace slag which fulfils these requirements is marketed under the trade name "NEWCEM" by the Blue Circle Cement Company. This slag is obtained from the Bethlehem
35 Steel Corporation blast furnace at Sparrows Point, Maryland.

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A usual blast furnace slag composition range in weight percent is: SiO_2 , 30-40; Al_2O_3 , 8-18; CaO , 35-50; MgO , 0-15; iron oxides, 0-1; S, 0-2 and manganese oxides, 0-2. A typical specific example is: SiO_2 , 36.4; Al_2O_3 , 16.0; CaO , 43.3; MgO , 3.5; iron oxides, 0.3; S, 0.5; and manganese oxides, < 0.1.

Blast furnace slag having relatively small particle size is frequently desirable because of the greater strength it imparts in many instances to a final cement. Characterized in terms of particle size the term "fine" can be used to describe particles with a specific surface area between 4 000 and 7 000 cm^2/g , corresponding to 16 to 31 micrometer in size; "microfine" can be used to describe those particles with a specific surface area in the 7 000 to 10 000 cm^2/g range that correspond to particles of 5.5-16 micrometer in size and "ultrafine" can be used to describe particles with a specific surface area over 10 000 cm^2/g that correspond to particles 5.5 micrometer and smaller in size. Small particle size blast furnace slags are available from Blue Circle Cement Co., Koch Industries, Tulsa, Oklahoma, under the trade name "WELL-CEM", and from Geochem under the trade name "MICROFINE MC100".

However, it is very time consuming to grind blast furnace slag to these particles sizes. It is not possible to grind blast furnace slag in a manner where particles are entirely one size. Thus, any grinding operation will give a polydispersed particle size distribution. A plot of particle size versus percent of particles having that size would thus give a curve showing the particle size distribution.

In accordance with a preferred embodiment of this invention a blast furnace slag having a polydispersed particle size distribution exhibiting at least two nodes on a plot of particle size versus percent of particles in that size is utilized. It has been found that if only a portion of the particles are in the ultrafine category, the remaining, indeed the majority, of the slag can be ground more coarsely and still give essentially the same result as is obtained from the more expensive grinding of all of

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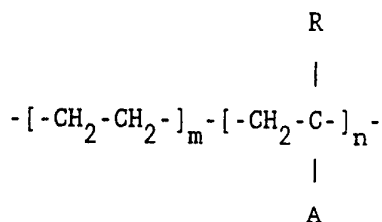
the blast furnace slag to an ultrafine state. Thus, a grinding process which will give at least 5% of its particles in a size range of 1.9 to 5.5 micrometer offers a particular advantage in economy and effectiveness. More preferably, 6 to 25wt% would fall in the 1.9 to 5.5 micrometer range. The most straightforward way of obtaining such a composition is simply to grind a minor portion of the blast furnace slag to an ultrafine condition and mix the resulting powder with slag ground under less severe conditions. Even with the less severe conditions there would be some particles in the fine, microfine or ultrafine range. Thus, only a minority, i.e., as little as 4wt% of the slag, would need to be ground to the ultrafine particle size. Generally, 5 to 25wt%, more preferably 5 to 10wt% can be ground to the ultrafine particle size and the remainder ground in a normal way thus giving particles generally in a size range of greater than 11 micrometer, the majority being in the 11 to 31 micrometer range.

Suitable activators include lithium hydroxide, lithium carbonate, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium hydroxide, magnesium oxide, magnesium silicofluoride, zinc carbonate, zinc silicofluoride, zinc oxide, sodium carbonate, titanium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, potassium sulphate, potassium nitrite, potassium nitrate, calcium hydroxide, sodium sulphate, copper sulphate, calcium oxide, calcium sulphate, calcium nitrate, calcium nitrite, and mixtures thereof. A mixture of caustic soda (sodium hydroxide) and soda ash (sodium carbonate) is preferred because of the effectiveness and ready availability. When mixtures of alkaline agents such as caustic soda and soda ash are used the ratio can vary rather widely since each will function as an accelerator alone. Preferably, about 3 to 57 kg/m³ of caustic soda, more preferably 6 to 18 kg/m³ of caustic soda are used in conjunction with from 6 to 143 kg/m³, preferably 6 to 60 kg/m³ of soda ash.

By ionomer is meant organometal compositions having a metal attached to or interlocking (cross-linking) a polymer chain or

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chains. Suitable polymer components of such ionomers can be represented by the formula:



wherein A is a carboxylic group, a sulphuric acid group, a phosphoric acid group or a mixture of a carboxylic group and a
 5 amide group, and wherein R is H or a 1-10 carbon atom alkyl radical. The ratio of m to n is generally between 0:1 and 100:1, preferably 0.1:1 and 10:1.

The polymers generally have a ratio of functional groups to polymer chain carbons between 1:2 and 1:10, preferably about 1:3.
 10 Thus, if m and n are 1, R is H and A is carboxylate, there would be a ratio of carboxylic carbons (1) to polymer chain carbons (4) of 1:4. The polymer can also be a polycarboxylic acid polymer. Another polymer is that made from partially hydrolyzed polyacrylamide. The hydrolysis can vary from 1% up to 100% and preferably from 10% to
 15 50%, most preferably from 25% to 40%. The molecular weight of the polymers can vary widely so long as the polymers are either water-soluble or water-dispersable. The weight average molecular weights can be between 1 000 and 1 000 000 but preferably will be between 1 000 and 250 000, most preferably 10 000 and 100 000.
 20 Carboxylate polymer with a low ratio of COOH:C between 1:3 and 2:5 are preferred. Especially preferred is a carboxylic acid polymer having a ratio of carboxylic carbons to polymer chain carbons (including carbons of pendant chains) of about 1:3 and a molecular weight between 10 000 and 100 000. Partially hydrolyzed
 25 polyacrylamide polymers having a molecular weight between 5 000 and 15 000 000 are suitable. The copolymers will generally have from 2-99, preferably 5-80, more preferably 10-60 mole percent acid-containing units.

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The poly(carboxylic acid) component can be any water soluble or water dispersable carboxylic acid polymer which will form ionomers. Ionomer forming polymers are well known in the art. Suitable polymers include poly(acrylic acid) poly(methacrylic acid), poly(ethacrylic acid), poly(fumaric acid), poly(maleic acid), poly(itaconic acid) and copolymers such as ethylene/acrylic acid copolymer and ethylene/methacrylic acid copolymer. The copolymers are generally random copolymers. An example of phosphonic acid polymers is poly(vinyl phosphonic acid) which is made from vinyl phosphonic acid, $\text{CH}_2=\text{CH}-\text{PO}_3\text{H}_2$.

Suitable copolymers containing vinyl phosphonic acid include vinyl phosphonic acid/acrylic acid copolymer as well as copolymers with other unsaturated monomers, with or without a functional group.

In some instances, it is preferred to use water dispersable, as opposed to water soluble, polymers. Ideally, in such instances the melting point of the polymer should be higher than the placement temperature (circulating temperature) in the borehole during the "cementing" operation and lower than the maximum, static temperature of the surrounding formations. It is desirable for the polymer to melt and react with the metal oxide component after placement as the temperature in the borehole increases from the circulating temperature to the static temperature of the surrounding formations.

The ionomers suitable for use in this invention are the water-insoluble reaction product of a proton accepting metal compound which serves as the cementitious component and a carboxylic, sulphonic, or phosphonic acid polymer component. The metal compound generally is a metal oxide such as CaO , MgO or ZnO . The preferred metal oxides are magnesium oxide and zinc oxide, and most preferably, magnesium oxide. The applicable metal oxides are generally fired at temperatures above 540°C for several hours to reduce chemical activity prior to grinding to final particle size for use in reacting with the acid component.

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In instances where it is desired that the metal compound component add weight to the drilling fluid, the metal compound is preferably a water-insoluble metal compound with a specific gravity of at least 3.0, preferably 3.5. By 'insoluble' is meant that less than 0.01 parts by weight dissolve in 100 parts by weight of cold (room temperature) water.

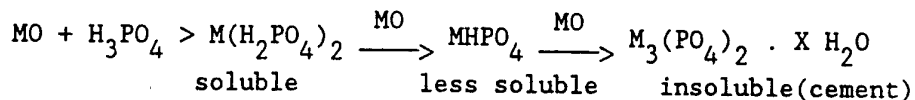
The amount of polymer utilized will vary widely depending upon the carboxylic acid content of the polymer; broadly, 10 to 200, preferably 10 to 100, most preferably 10 to 80wt%, based on the weight of metal compound, can be present. With the polymers having a low ratio of m to n, a smaller amount is required because of the higher functional group content of the polymer. Conversely, with the high ratio of m to n, an amount of polymer toward the higher end of the ranges is preferred.

Phosphates and phosphonates, referred to herein as phosphorus salts, used in accordance with this invention also are produced from a two-component composition, the first component of which is a metal compound identical in scope to that used in the ionomers as described hereinabove so long as the resulting phosphorus salt is insoluble in water. Most preferred are CaO, MgO and ZnO.

The second component is a phosphonic or phosphoric acid, preferably a polyphosphoric acid. The term 'phosphoric acid' is meant to encompass both linear and cyclic polyphosphoric acids. These second component acids are referred to herein as phosphorus acids. Linear phosphoric acids can be depicted by the general formula $H_{n+2}P_nO_{3n+1}$ where n is 1 to 100, preferably 2 to 50, more preferably, 2 to 20. Examples include di-(pyro)phosphoric acid, tri-(tripoly)phosphoric acid, tetra-phosphoric acid and higher molecular weight polyphosphoric acids as well as phosphoric acid. Mixtures of acids, including those traditionally referred to as meta phosphoric acid, are particularly suitable for use in this invention.

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The formation of one phosphate cement using a metal oxide as the metal compound can be depicted as follows:



where:

X is usually 4; and

5 MO = metal oxide which is amphoteric or is a proton accepting metal compound. /

With the ionomers, and the phosphorus salts when made with a polyvalent metal compound, a cross-linked network structure exists as a result of the addition of the second component, thus giving a very strong solid cement.

The particle size of the metal compound component can vary widely. Generally, it will be in a range such that the powder exhibits a surface area between 1 000 cm²/g and 30 000 cm²/g, preferably 1 500 cm²/g and 25 000 cm²/g, most preferably 2 000 cm²/g and 20 000 cm²/g.

The phosphorus acid is generally used in a stoichiometric amount or less, since an excess should generally be avoided. From 1 to 10 or even 1 to 50 mole percent less than a stoichiometric amount is suitable. Generally, a stoichiometric amount will be between 10 and 100 weight percent based on the weight of the metal compound.

Because of the mass provided by the metal compound component of the ionomer or the polyphosphorus salt, these cementitious materials are generally actually heavier than most slag or Portland cement materials. In the embodiments using these cementitious materials this high density provides significant advantages in certain utilities. For one thing, a smaller amount of the material can be used and still achieve a final drilling fluid and ultimately cementitious slurry of a desired density. Secondly, because of the high density, it is possible to operate without weighting agents such as barium sulphate or barite. They offer a further advantage in that they do not set up until the second component is added.

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The metal compound of the ionomer or phosphorus salt can be used as the sole cementitious material or can be used in admixture with siliceous hydraulic materials such as the blast furnace slag or Portland cement. In one embodiment an hydraulic component such as blast furnace slag can be used to give the metal ion component of the ionomer or phosphate to give, in effect, a mixture formed in situ.

Preferably, when the ionomer or phosphorus salt is utilized, the metal compound is added first and thereafter at such time as it is desired for the cement to be activated to set, the other component is added. In the case of the universal fluids, a portion of the total metal compound can be added to the drilling fluid, the remainder being added when the cementitious slurry is being formed.

The preferred sequence for universal fluid in this embodiment of the invention is to prepare the drilling fluid containing a portion of the total slag or metal compound to be utilized, carry out the drilling operation, dilute the fluid, add the remainder of the slag or metal compound, and thereafter add the acid components and utilize the cement for its intended purpose such as cementing a casing.

Generally, the used universal fluid will be diluted and more cementitious material added as well as the reactive second component when the cementitious slurry is formed. Dilution of the drilling fluid is usually needed for control of the density and rheology of the final cementitious slurry. The amount of dilution can vary widely depending on the desired application. Generally, the fluid will be diluted with from 5 to 200%, preferably 5 to 100%, more preferably 5 to 50% by volume (water in the case of a water-based fluid) per volume of initial drilling fluid. In one particularly preferred embodiment, the dilution is such that on addition of the cementitious component (or in the case of the universal fluid addition of the remaining cementitious component) the final density will be between 30% less and 70% more than the original density, preferably between 15% less and 25% more, most preferably, essentially the same, i.e., varying by no more than

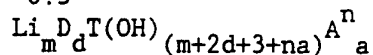
- 17 -

+5 wt%. This is particularly valuable in an operation where there is a small difference between the pressure needed to prevent blowout and the pressure which would rupture or fracture the formation through which drilling has taken place.

5 The dilution fluid can be the same or different from that used to make the drilling fluid initially. In the case of brine-containing fluids the dilution fluid will generally be brine also. This is of particular benefit in offshore drilling operations where fresh water is not readily available but seawater is abundant.

10 Preferably, the dilution is carried out "on the fly" by adding dilution fluid to a flowing stream of the used drilling fluid and thereafter adding the additional ingredients.

In some instances it is desirable to sequence the incorporation of ingredients into the drilling fluid. For instance, with slag as the cementitious component, it may be desirable to introduce and mix thinners and/or retarders and activators and thereafter introduce the slag. This is particularly true if mixed metal hydroxides are used in the drilling fluid to impart thixotropic properties. The mixed metal hydroxides provide better solids suspension. This, in combination with the settable filter cake provided in the technique of this invention, greatly enhances the cementing in a restricted annulus. The mixed metal hydroxides are particularly effective in drilling fluids containing clay such as sodium bentonite. Preferred systems thickened in this way contain from 3 to 57 kg/m³ of clay such as bentonite, preferably 6 to 43 kg/m³, most preferably 20 to 34 kg/m³. The mixed metal hydroxides are generally present in an amount between 0.3 and 6 kg/m³ of total drilling fluid, preferably 0.3 and 4 kg/m³, most preferably 2 and 4 kg/m³. Mixed metal hydroxides are known in the art and are trivalent metal hydroxide-containing compositions such as MgAl(OH)_{4.7}Cl_{0.3}. They conform essentially to the formula



where

m represents the number of Li ions present; the amount being between 0 and about 1;

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D represents divalent metals ions; with
d representing the amount of D ions between 0 and about 4;
T represents trivalent metal ions;
A represents monovalent or polyvalent anions of valence n, other
5 than OH^- , with a being the amount of A' anions; and
where $(m+2d+3+na)$ is equal to or greater than 3.

A more detailed description can be found in USA patent
specification No. 4 664 843. The mixed metal hydroxides in the
drilling fluid, in combination with blast furnace slag, tend to set
10 to a cement having considerable strength in a comparatively short
time, i.e., about one-half hour at temperatures as low as 38 °C.
This can be a major asset in some applications. In such instances,
a thinner such as a lignosulfate is preferably added before adding
slag. However, one of the advantages of this invention is that it
15 reduces or eliminates the need for additives to control free water
or solids suspension. The activator or activators can be added
either before or after the addition of the additional blast furnace
slag.

In some instances, it may be desirable to use a material for a
20 particular effect along with the activator even though it may also
act as a retarder. For instance, a chromium lignosulphonate may be
used as a thinner along with the activator even though it also
functions as a retarder.

Other suitable thinners include chrome-free lignosulphonate,
25 lignite, sulphonated lignite, sulphonated styrene maleic-anhydride,
sulphomethylated humic acid, naphthalene sulphonate, a blend of
polyacrylate and polymethacrylate, an acrylamideacrylic acid
copolymer, phenol sulphonate, dodecylbenzene sulphonate, and
mixtures thereof.

30 In the case of blast furnace slag, the amount of slag present
in the universal fluid is generally between 3 and 300 kg/m^3 of
final drilling fluid, preferably 30 and 240 kg/m^3 , most preferably
60 and 150 kg/m^3 . In the case of the organometals (ionomers) or
phosphorus salts the amount of metal compound initially present in
35 universal fluid can also vary widely. Generally, between 3 and

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1 450 kg/m³, preferably 145 and 860 kg/m³, most preferably 290 and 715 kg/m³ of the metal compound are used.

5 The total amount of cementitious material in the cementitious slurry will typically be between about 60 and about 1 700 kg/m³, preferably 290 and 1 450 kg/m³, most preferably 450 and 1 000 kg/m³.

10 Reference herein to additives encompasses both the specialized additives necessary for this invention such as the carboxylic acid polymer in the case of the ionomer or the polyphosphoric acid in the case of the polyphosphate as well as conventional additives.

Conventional additives which can be added include accelerators, retarders, and other known components of cementitious materials.

15 Other additives which can be present in the drilling fluid include low and medium yield clays, carboxymethyl cellulose, polyacrylonitrile, natural gum, molecularly dehydrated phosphate, tannin compounds, quebracho, mined lignites, lignosulphonates broadly, mica, sugar cane fibres and granular materials. In addition to bentonite, amorphous and crystalline clays such as
20 kaolinite, halloysite, smectite, montmorillonite, illite, saconite, vermiculite, chlorite, attapulgite, sepiolite, palygorskite and Fuller's earth are useful in combination with mixed metal hydroxides.

25 In yet another related embodiment of this invention, universal fluid is utilized in a drilling operation and thereafter additional cementitious material and/or additives, or the second component of a two-component system, is gradually added so as to gradually change the circulating material from a drilling fluid to a cementitious slurry.

30 In yet another embodiment of this invention the drilling process is carried as described hereinabove with a universal fluid to produce a borehole through a plurality of strata thus laying down a filter cake. Prior to the cementing operation an activator or reactive second component is passed into contact with the filter
35 cake, for instance by circulating the activator or reactive second

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component down the drill string and up the annulus between the drill string and the filter cake, or else the drill string is removed and the casing inserted and the activator circulated down the casing and up the annulus. As used herein 'down' as it relates to a drill string or casing, means in a direction toward the farthest reach of the borehole even though in rare instances the borehole can be disposed in a horizontal position. Similarly, 'up' means back toward the beginning of the borehole. Preferably, the circulation is carried out by using the drill string, this being the benefit of this embodiment of the invention whereby the filter cake can be "set" to shut off gas zones, water loss, or to shut off lost circulation in order to keep drilling without having to remove the drill string and set another string of casing. This can also be used to stabilize zones which may be easily washed-out (salt zones wherein the salt is soluble in water, for instance) or other unstable zones. After the drilling is complete the drill string is removed, and the cementing carried out as described hereinabove. This can be accomplished by circulating a separate fluid containing the activator or by adding an activator such as an alkali as described hereinabove to the drilling fluid.

Conventional spacers may be used in the above described sequence. Also, any left over fluid having activators therein may be displaced out of the borehole by the next fluid and/or a spacer fluid and stored for subsequent use or disposal.

In this embodiment where the filter cake is "set", the activator can be any of the alkaline activators referred to hereinabove such as a mixture of sodium hydroxide and sodium carbonate when the universal fluid contains slag. The reactive second component is a polymer with a functional group such as a carboxy group as described hereinabove wherein the universal fluid contains a proton accepting metal compound, or the phosphoric or phosphonic acid component of a phosphate or phosphonate when the universal fluid contains a proton accepting metal compound.

In another embodiment of this invention, the drilling is done using a drilling fluid containing a metal compound to lay down a

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filter cake which is preferably set as described above with a reactive second component and thereafter the cementing is done with a cementitious slurry comprising blast furnace slag, water and an accelerator.

5 Also, the use of blast furnace slag as described above for the metal compound source is applicable in this embodiment as well. Thus, an ionomer or phosphate salt can be formed as filter cake followed by cementing with blast furnace slag.

10 The invention is of particular value in cementing of large casings and liners as the following Example shows. By 'large' is meant 30- to 75-cm, generally 41-cm or greater outside diameter.

The invention will now be described in more detail with reference to the below examples.

15 To illustrate the known method of drilling and cementing a well, eight separate 41-cm casings were set in boreholes drilled using a conventional drilling fluid having the following composition: 10-20 wt% salt, 23-30 kg/m³ bentonite, 11-18 kg/m³ carboxymethyl starch (fluid loss preventor), sold under the trade name "BIOLOSE" by Milpark, 1.4-2.8 kg/m³ partially hydrolyzed
20 polyacrylamide (PHPA) which is a shale stabilizer, sold under the trade name "NEWDRIIL" by Milpark, 2.8-3.5 kg/m³ CMC sold under the trade name "MILPAC" by Milpark, 86-200 kg/m³ drill solids, and 0-715 kg/m³ barite.

25 The drilling fluid was displaced with a 1 960 kg/m³ Class H Portland cementitious slurry. The cementitious slurry was forced down the casing in a manner shown in Figure 1 herein using a wiper plug followed by additional drilling fluid (Figure 1 differs in that it depicts cementing a liner whereas the examples not according to the invention involve cementing a casing). All 8 of
30 the casings failed a standard 13.8 MPa (gauge) pressure test indicating a poor cementing job, which would suggest that the wiper plug seal against the landing collar had failed and that part of the additional drilling fluid could pass the seal and mix with the cementitious slurry in the annulus.

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Example 1: In experiments to test this invention an identical 41-cm casing was set in a borehole drilled with identical drilling fluid to that described in the Control. A cementitious slurry was made by combining drilling fluid of the type used in the drilling
5 with blast furnace slag activators and additives. Two separate batches were prepared; one for the lead part of the cementing and one for the tail part. A sample of each was taken prior to their use for the purpose of determining the properties of the cementitious slurry and the compressive strength of a test specimen
10 made from each sample using the temperature anticipated for the bottom of the borehole.

The drilling fluid volume refers to m^3 of drilling fluid per m^3 of final cementitious slurry whereas the other ingredients are listed in terms of kg per m^3 of final cementitious slurry. These
15 are set out hereinbelow.

Table 1. Data of the compositions of the fluids used in Example 1.

Slag-Mix Type	Lead	Tail
Slurry Density, kg/m ³	1 617	1 833
Mud Density, kg/m ³	1 341	1 341
Mud volume, m ³ /m ³ cement	0.81	0.08
SPERCENE CF ¹ , kg per m ³ cement	2.3	--
UNICAL CF ² , kg per m ³ cement	--	7.1
NaOH, kg per m ³ cement	14	14
Na ₂ CO ₃ , kg per m ³ cement	28	14
NEWCEM ³ , kg per m ³ cement	485	856
Rheology at 21 °C		
Plastic viscosity, mPa.s	19	75
Yield point, Pa	1.4	11
10-sec. gel strength, Pa	1.4	9.6
10-min. gel strength, Pa	6.7	34
Bottom Hole Static Temperature, °C	38	41
Compressive Strength, MPa	13	36

¹ "SPERCENE CF" is a trade name of M-I Drilling Fluids for chrome lignosulphonate.

² "UNICAL CF" is a trade name of Milchem for chrome-free lignosulphonate.

5 ³ "NEWCEM" is ground blast furnace slag of about 5 500 specific surface area available from Blue Circle Cement Co.

The blast furnace slag cementitious lead slurry was introduced into the casing displacing the drilling fluid. The lead slurry was followed by the tail slurry in order to leave a high strength
 10 cement around the casing shoe. The tail slurry was then displaced down the casing by direct contact of a measured volume of drilling

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fluid against the top of the cementitious slurry column as shown in Figure 2. The casing was given the same standard 13.8 MPa (gauge) pressure test and passed.

5 This shows that using direct fluid contact in accordance with the technique of this invention not only simplifies the procedure by eliminating the wiper plug but gives better results.

Two additional experiments were carried out under essentially identical conditions with the same satisfactory results.

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C L A I M S

1. A method for drilling and cementing a well, comprising:
drilling a borehole utilizing a drilling fluid, thus producing
a used drilling fluid;
combining ingredients comprising water, blast furnace slag and
5 an activator to produce a cementitious slurry;
disposing a pipe in the borehole;
passing the cementitious slurry down the pipe; and
displacing the cementitious slurry up into an annulus
surrounding the pipe through direct contact by a displacement
10 fluid.
2. The method according to claim 1 wherein the water of the
cementitious slurry contains dissolved salts.
3. The method according to claim 2 wherein the water of the
cementitious slurry is seawater.
- 15 4. The method according to claim 1 wherein the activator is
selected from the group consisting of sodium silicate, sodium
fluoride, sodium silicofluoride, magnesium silicofluoride,
magnesium hydroxide, magnesium oxide, zinc silicofluoride, zinc
oxide, zinc carbonate, titanium carbonate, sodium carbonate,
20 potassium sulphate, potassium nitrate, potassium nitrite, potassium
carbonate, sodium hydroxide, potassium hydroxide, copper sulphate,
lithium hydroxide, lithium carbonate, calcium oxide, calcium
nitrate, calcium nitrite, calcium hydroxide, sodium sulphate and
mixtures thereof.
- 25 5. The method according to claim 1 wherein 5 to 25 wt% of the
blast furnace slag has an ultrafine particle size.
6. The method according to claim 1 wherein the drilling fluid
contains seawater, the activator is a mixture of sodium hydroxide
and sodium carbonate, and wherein 5 to 25 wt% of the blast furnace
30 slag has an ultrafine particle size.

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7. The method according to claim 1 wherein the cementitious slurry is prepared by combining the used drilling fluid with the blast furnace slag and wherein the activator is a mixture of sodium hydroxide and sodium carbonate, and wherein the cementitious slurry
5 contains 400 to 1 000 kg/m³ of the cementitious material and wherein the pipe has a diameter of 40 cm or greater.
8. The method according to claim 7 wherein the displacement fluid comprises seawater.
9. The method according to claim 1 wherein the pipe is a casing
10 and the annulus is the annulus between the casing and the borehole.
10. The method according to claim 1 wherein the pipe is a liner and the annulus is the space between the liner and a casing.
11. A method for drilling and cementing a well, comprising:
combining blast furnace slag having a particle size between
15 2 000 and 15 000 cm²/g with an aqueous drilling fluid, the blast furnace slag being present in an amount between 2.8 and 280 kg/m³ of the drilling fluid plus blast furnace slag;
utilizing the drilling fluid in a well drilling operation to form a borehole to produce a used drilling fluid;
20 combining additional blast furnace slag and an activator with the used drilling fluid to produce a cementitious slurry;
disposing a pipe in the borehole;
passing the cementitious slurry down the pipe; and
displacing the cementitious slurry up into an annulus
25 surrounding the pipe by direct contact with a displacement fluid.
12. The method according to claim 11 wherein the activator is a mixture of sodium hydroxide and sodium carbonate, and wherein the displacement fluid comprises seawater.
13. A method for drilling and cementing a well, comprising:
30 combining constituents comprising water and a metal compound proton accepting component to produce a drilling fluid;
utilizing the drilling fluid in a well drilling operation to form a borehole, thus producing a used drilling fluid and laying down a filter cake;
35 contacting a reactive second component with the filter cake;

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disposing a pipe in the borehole after the filter cake is laid down;

passing a cementitious slurry down the pipe; and

displacing the cementitious slurry up into an annulus

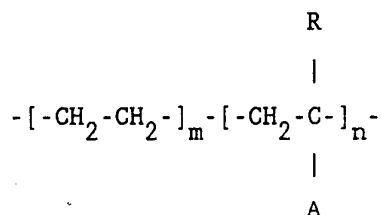
5 surrounding the pipe by direct contact with a displacement fluid.

14. The method according to claim 13 wherein the proton accepting metal compound is a metal oxide.

15. The method according to claim 13 wherein the proton accepting metal compound is magnesium oxide.

10 16. The method according to claim 13 wherein the proton accepting metal compound is supplied by blast furnace slag.

17. The method according to claim 13 wherein the reactive second component is selected from the group consisting of phosphonic acid, phosphoric acid, polyphosphoric acid and a polymer of the formula

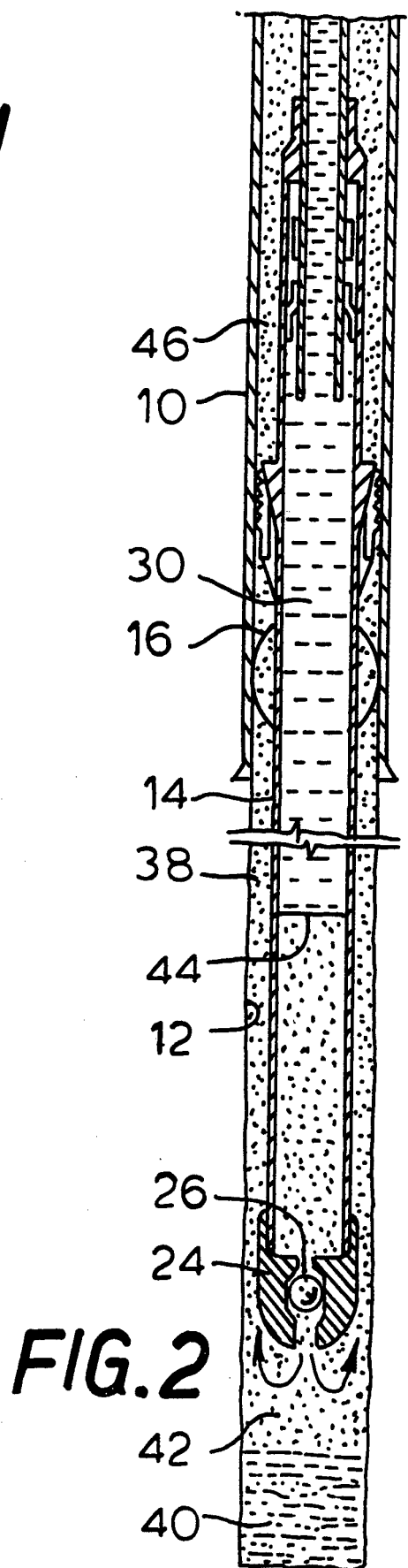
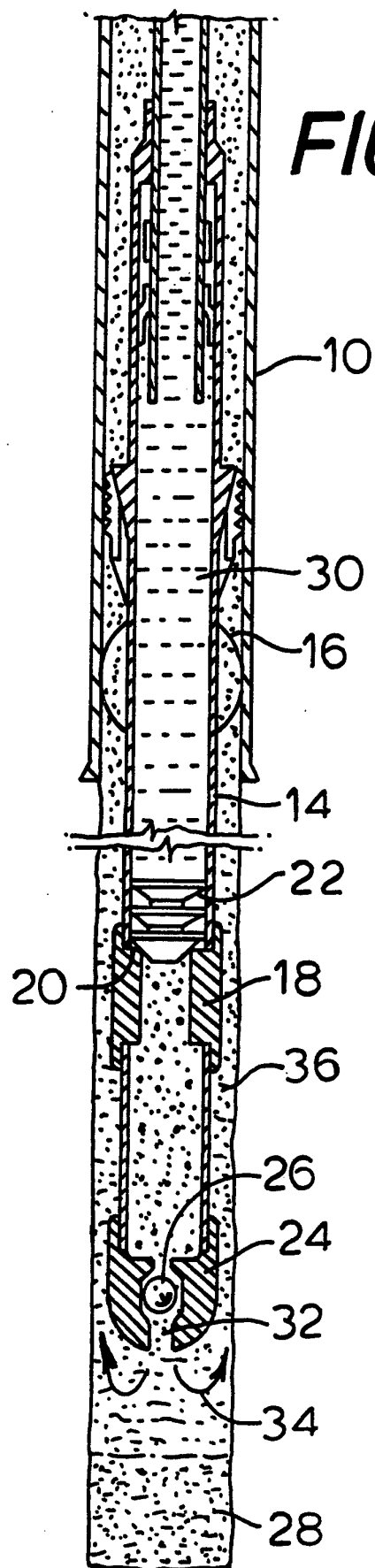


15 wherein A is a carboxylic group, a sulphuric acid group, a phosphoric acid group or a mixture of a carboxylic group and a amide group, and wherein R is H or a 1-10 carbon atom alkyl radical.

18. The method according to claim 17 wherein the reactive second component is poly(acrylic acid).

19. The method according to claim 13 wherein the cementitious slurry comprises blast furnace slag and water.

20. The method according to claim 13 wherein the cementitious slurry is prepared by combining a portion of the used drilling fluid with additional proton accepting metal oxide and additional
25 reactive second component.



INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 93/02929

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 E21B33/13

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 5 E21B C09K

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 058 679 (SHELL) 22 October 1991 see column 2, line 5 - column 4, line 37; claims 1-14 ---	1-16, 19, 20
A,P	US,A,5 213 160 (SHELL) 25 May 1993 see column 2, line 14 - column 6, line 58; claims 1-10 ---	1-16, 19, 20
A,P	EP,A,0 521 376 (GEOCHEMICAL CORPORATION) 7 January 1993 see page 3 - page 6, line 23 -----	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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 "&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 93/02929

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5058679	22-10-91	NONE	
US-A-5213160	25-05-93	NONE	
EP-A-0521376	07-01-93	US-A- 5106423	21-04-92
		AU-A- 1845692	07-01-93
		CA-A- 2072064	25-12-92