Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2072064 C 2003/10/14

(11)(21) 2 072 064

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(22) Date de dépôt/Filing Date: 1992/06/23
(41) Mise à la disp. pub./Open to Public Insp.: 1992/12/25
(45) Date de délivrance/Issue Date: 2003/10/14
(30) Priorité/Priority: 1991/06/24 (07/720,239) US

(51) Cl.Int.^{5}/Int.Cl.^{5} C09K 7/04, E21B 33/138
(72) Inventeur/Inventor:
CLARKE, WILLIAM J., US

(73) Propriétaire/Owner:
SCHLUMBERGER TECHNOLOGY CORPORATION, US

(74) Agent: SMART & BIGGAR

(54) Titre : METHODE DE CIMENTATION AU MORTIER LIQUIDE DE FORMATIONS GAZEIFERES ET PETROLIFERES

(54) Title: METHOD OF GROUTING POROUS GAS - AND PETROLEUM - BEARING FORMATIONS

(57) Abrégé/Abstract:
A method of grouting porous gas - and petroleum - bearing formations with a cementitious material (40) comprising ultrafine ground slag is useful for primary and remedial cementing of a wellbore (37). A composition is provided which comprises water, a dispersant, slag and an accelerator to activate the slag.

2072064

A B S T R A C T

A method of grouting porous gas - and petroleum - bearing formations with a cementitious material (40) comprising ultrafine ground slag is useful for primary and remedial cementing of a wellbore (37). A composition is provided which comprises water, a dispersant, slag and an accelerator to activate the slag.

71456-148

METHOD OF GROUTING POROUS GAS - AND PETROLEUM - BEARING FORMATIONS

This invention relates to a method of grouting porous gas - and petroleum - bearing formations. The invention also relates to a composition suitable for use in the method of the invention. The method and composition of the invention are particularly useful for preventing permeation of water.

The present method utilizes a MICROFINE* (ultrafine ground) slag as a component of an economical grouting composition having an excellent combination of properties for the above-mentioned uses. It has earlier been proposed in D. W. Moller, H.L. Minch, J.P. Welsh, "Ultrafine Cement Pressure Grouting to Control Ground Water in Fractured Granite Rock" ACI Proceedings, SP 83-8, Fall Convention, Kansas City, 1983, and in W.J. Clarke, "Performance Characteristics of Microfine Cement", ASCE preprint 84-023, Geotechnical Conference, Atlanta, May 14-18, 1984, to use ultrafine ground cement for underground strengthening and water control. The cement proposed for such use was a co-ground combination of slag and portland cement having fineness properties of a specific surface area of 8,880 cm^2/g and a grain size of about 50% of particles below about 4 micrometers.

The use of more finely divided slag having a

*Trade-mark

specific surface area greater than 9,500 cm^2/g in a composition for sealing, stabilizing and strengthening formations is described in U.S. Patent 4,761,183 granted on August 2, 1988 to the present applicant.

Forss U.S. Patent 4,306,912 issued on December 22, 1981, describes the activation of slag by use of an accelerator comprising sodium hydroxide.

U.S. Patent 4,897,119 granted on January 30, 1990 to the present applicant, describes dispersants useful for ultrafine ground slag grouting compositions.

"Worldwide Cementing Practices", Dwight K. Smith, 1991, American Petroleum Institute, Johnston Printing Company, Dallas, Texas; "Well Cementing", Erik, B. Nelson, 1990, Elsevier Science Publishers, Amsterdam; and "Cementing", Dwight K. Smith, 1990, Society of Petroleum Engineers, New York, disclose techniques for cementing wells and gas - and oil - bearing formations, especially the use of portland cement for such purposes and cement additives.

According to the present invention there is provided a method of grouting porous gas - and petroleum - bearing formations, which comprises injecting into the formation or a wellbore, a composition comprising a particulate slag, the composition comprising:

a. water

b. particulate slag, having a specific surface area greater than about 9,500 cm^2/g, with less than 3 wt. percent of the particles of the slag being larger than 7.8 micrometers in diameter; the proportions of water and slag being within a water to slag weight ratio range of between 0.3:1 and 10:1;

c. at least one dispersant in an amount

effective to disperse the particles of the particulate slag; and

d. an accelerator in an amount effective to provide hydraulic reactivity to the slag.

In a further method aspect, the invention provides a method of grouting a porous gas - and petroleum - bearing formation, which comprises injecting into the formation a composition comprising: (a) water; (b) particulate slag having a specific surface area greater than about 11,000 cm^2/g, with less than 1.5 wt. percent of the particles of the slag being larger than 7.8 micrometers in diameter the water and the slag being in such proportions that a water to slag weight ratio is between 0.3:1 and 10:1; (c) at least one dispersant in an amount effective to disperse the particles of the particulate slag; and (d) an accelerator in an amount effective to provide hydraulic reactivity to the slag.

There is a need in well cementing procedures to provide a method of grouting formations which achieves high permeation of grout into the formation with a grout which has desired setting, hardening and settlement properties.

Because of the large quantities of grouting composition which must be employed when used to stabilize or strengthen formations or to contain water in such formations, the grouting composition not only must possess the desired combination of properties, but also needs to be economical.

The present invention provides a method of grouting which enables the sealing of a formation such that the formation attains a very low permeability to water and other fluids and thus is useful for oil well cementing. Compositions used in the present invention have an unusual ability to penetrate such formations and have desirable characteristics of setting and hardening time. These compositions also are economical and non-polluting.

In a composition aspect, the invention provides a grouting composition for grouting a porous gas - and petroleum - bearing formation or a wellbore formed in the formation, which composition comprises: (a) water; (b) a particulate slag which is a ultrafine slag having a specific surface area greater than about 10,000 cm^2/g with less than 3 wt. percent of the particles of the slag being larger than 7.8 micrometers in diameter, the water and slag being in such proportions that a water to slag weight ratio is between 0.5:1 and 2:1; (c) at least one dispersant in an amount effective to disperse the particles of the particulate slag; and (d) an accelerator in an amount effective to provide hydraulic reactivity to the slag.

In the drawings:

Fig. 1 is a ternary phase diagram showing the relative proportions of calcium, aluminum and silicon oxides in cements, slag and related products.

Fig. 2 is a diagrammatic sectional illustration of tube-a-machette grout injection.

The following Table 1 illustrates examples of the chemical composition of portland cement, M5 slag/cement and M1 slag.

TABLE 1

	PORTLAND	M5	M1
SiO_2	22.	30.6	35.4
Al_2O_3	5.2	12.4	16.
Fe_2O_3	3.2	1.1	0.3
CaO	65.2	48.4	43.3
MgO	1.3	5.8	3.5
SO_3	1.9	0.8	0.3

As is shown in Table 1 and in the ternary diagram of Fig. 1, portland cement is high in calcium oxide and low in silicon dioxide while M1 slag contains a lower content of calcium oxide and a higher content of silicon dioxide. The composition of M5 slag/cement is between that of portland and M1 slag. In the United States Geochemical Corporation markets ultrafine cement under the trademark MICROFINE, and sells M5 slag/cement under the trademark MC-500 and M1 slag under the trademark MC-100.

The major advantage of MICROFINE cement over portland is the ability to permeate fine sands and finely cracked rock. M1 and M5 permeate fine sands while portland does not permeate coarse sand. This provides the justification for using MICROFINE cement for permeation grouting dam curtains, stabilizing hazardous wastes and containment of nuclear wastes.

Permeation testing has showed that M1 MICROFINE cement permeates fine sand at 3 times the volume of M5. This indicates that particulate grouts with particle size one third the fine sand openings operate like solution grouts where most of the particles pass through the sand.

Low viscosity is required for fast permeation of the MICROFINE cements. This is provided by higher water/cement weight ratios (above 1:1) and the use of dispersants. The viscosity of all water ratios of M1 or of M5 are lower than portland. At 2:1 water to cement ratio the viscosity of M1 and of M5 is 7 and 9 centipoises, respectively. Lower water/cement (WC) ratios (water below 1:1) are usable in coarser formations using higher pressure injection to obtain low formation permeability for hazardous waste containment.

Permeability of neat MICROFINE and portland cements were laboratory tested by taking samples of hazardous waste water and determining the permeability of the neat (no sand content) cement to the waste water. Permeability rates through M1 are very low at 10^{-9} cm/sec after 15,000 minutes. M5 gave almost 10^{-9} and portland gave lower than 10^{-7} cm/sec permeability. These low permeability rates indicate that M1, M5 or M1 plus M3 (MICROFINE portland) MICROFINE cements may be used in well cementing, to contain nuclear wastes and to stabilize hazardous waste plumes.

The grouting composition used in the present invention comprises an ultrafine slag, water in which the slag is dispersed, a dispersant and an accelerator which increases the hydraulic reactivity of the slag.

The ultrafine slag is a cementitious material (CM) having a specific surface area (SSA) greater than 9,500, preferably greater than 11,000 and most preferably greater than 13,000 or 14,000 square centimeters per gram and, by weight, less than 3%, preferably less than 1.5% and most preferably no particles of the slag larger than 7.8 micrometers in diameter. Especially for well cementing applications, it is preferred that the MICROFINE slag has less than 2 wt. percent particles larger than 10 microns in diameter. (The surface area and particle size are measured by the use of the Microtrac R instrument further described hereinbelow.)

An optional cementitious material in the composition is cement having an SSA greater than 6,000 cm^2/g, or better, greater than 8,000 cm^2/g. Still better such cement has an SSA greater than 10,000, preferably greater than 11,000, with, by weight, less than 16%, preferably less than 7% and most preferably less than 3% of particles of the cement larger than 7.8 micrometers in diameter as measured by the Microtrac R instrument. The preferred optional cement is portland cement. When used, preferably the optional cement has an SSA of at least about 9,000 cm^2/g, more preferably 10,000 about cm^2/g and is mixed with ultrafine slag having an SSA of at least about 14,000 cm^2/g, the mixture having an SSA of at least about 12,000 cm^2/g. It is particularly preferred, especially for gas - and petroleum well cementing, with MICROFINE slag, to additionally use portland cement having a particle size wherein less than 2 wt. percent of the particles of said portland cement are larger than 10 microns in diameter, the slag being at least 40 percent by weight of the total of portland cement and slag.

The hydration of slag differs from that of portland cement in many aspects. The most striking difference is that slag powder is a homogenous material (glass) with a rather uniform reactive surface, while clinker powder is largely inhomogeneous. The clinker powder is composed of small areas of various minerals with highly different solubilities and reactivities. The reaction with water is highly exothermic and the hydrated structure is built up from a needle-like structure. The reaction between slag-glass and water is only slightly exothermic, and the hydrated structure is built up from a rather homogeneous mass. To be able to reach high early strength the particles in a hydrating body containing slag need to be very close. One way this is made possible is by reducing water content in all types of slag-bearing hydrating bodies.

The WC weight ratio in the present invention is from 0.5:1 to 10:1. For low formation permeability in water control and hazardous waste containment a WC ratio of 0.5:1 to 2:1 is employed. For formation strengthening applications a WC ratio of 1:1 to 10:1 is preferred. For grouting gas - and petroleum - bearing formations and wellbores, a WC ratio of 0.5:1 to 10:1 may be employed and for many such applications a ratio of 0.5:1 to 1.5:1 is preferred. Also a ratio of 0.3:1 to 10:1 may be employed, and preferably 0.4:1 to 1.5:1.

Additional materials in the grout are a dispersant, an accelerator and optional additives, the amounts of these described below being in weight percent solids based on the weight of cementitious material (CM) unless otherwise noted.

An effective amount of dispersant to disperse the CM may be up to 2%, and is preferably 0.1% to 1%, more preferably 0.2% to 0.5%. In grouting gas - and petroleum - bearing formations it is important to control viscosity of cement slurry which is being injected to facilitate pumping and penetration at increasing depths of the wellbore. Increased viscosity adversely affects penetration of cement into the formation. In this invention, it has been found that use of up to 2 percent by weight (based on cement) of a naphthalene sulfonate formaldehyde condensate (N2) as dispersant is effective to reduce viscosity and to provide desired control of viscosity. Furthermore, N2 has water loss reducing properties. Dispersants include polymers and lignosulfonates.

Also in such well cementing operations, it is necessary to avoid early set and hardening times which interfere with pumping and penetration at increased wellbore depths. Where this is a problem it is preferred to add an amount of a retarder effective to obtain desired longer set and hardening times. Retarders include lignins, gums, starches, weak organic acids and cellulose derivatives such as carboxymethyl hydroxyethyl cellulose. Some dispersants such as N2 and lignosulfonates also act as retarders.

Silica flour (finely ground silica) may be added in a proportion where the silica flour is not more than 50 percent of the total weight of silica flour, particulate slag and portland cement. The resulting composition is useful because of advantages of increasing compressive strength and durability.

To obtain the combined properties desired in the method of the present invention, it is essential to include an accelerator, in an effective amount to initiate or give the ultrafine slag sufficient hydraulic reactivity so that it sets and hardens in desired times, depending on the proposed applications. The accelerator may comprise an alkali or alkaline earth oxide, hydroxide or salt, which imparts the desired hydraulic reactivity to the ultrafine slag, or may comprise any other substance which is effective to provide or improve the hydraulic reactivity of the slag. NaOH is a preferred accelerator, particularly when used in an amount of 5 to 10% by weight of CM. NaOH may be used with optional further additives, such as sodium carbonate, to enhance the activation effect. It has been found that substitution of up to 40% by weight of the sodium hydroxide by Na_2CO_3 is very effective, and preferably up to 20% of the NaOH is substituted. Such optional further additives also may be selected from alkali or alkaline earth oxides, hydroxides or salts, or from any other compound which functions to activate the slag. Also preferred as an optional further additive are alkali metal polysilicates, such as a lithium sodium polysilicate or a lithium polysilicate. Another optional further additive is sodium fluoride, which may be used in amounts up to 2%, preferably up to 1%, more preferably 0.1 to 0.5% by weight of the CM.

When an optional cement is used with the slag, particularly portland cement, in effect the accelerator is at least partly comprised therein due to the CaO content of the cement being capable of activating the slag. Thus, in some formulations in which a cement is mixed with the slag, a separate accelerator such as NaOH may be omitted. However, although the formulations using a mixture of slag and cement without a separate accelerator can have low set time and low settlement, hardening time may be substantially increased. Where such an increase is found, and a shorter hardening time is needed for the particular application, a separate accelerator may be used with the slag-cement mixture.

The slag employed in this invention is a by-product obtained in the blast furnace process of smelting iron ore to produce iron. The slag is produced by a conventional process, utilizing grinding and separating steps well known in the art. A typical dry composition range and two further examples of slag are shown in Table 2 (in weight percent):

TABLE 2

Composition	SiO_2	Al_2O_3	CaO	MgO	FeO	S	Mn_2O_3
Usual Range	30-40	8-18	35-50	0-15	0-1	0-2	0-2
Typical	36.4	16.0	43.3	3.5	0.3	0.5	<0.1
Typical	35.5	11.4	39.4	11.9	0.2	0.2	-

A high glass content, finely divided slag yields a grout having excellent sulfate resistance and readily controlled setting and hardening times in a relatively inexpensive formulation. High sulfate resistance is particularly important with regard to long term stability of the grouted formation. Grouting failures after five or ten years have been attributed to sulfate attack. The slag rich compositions of the present invention have long term stability in formations and are also useful in regrouting formations in which a previous grout has exhibited signs of failure. The grout is inexpensive because of the comparatively low cost of slag, a by-product of iron production.

Properties of specific types of MICROFINE cements which can be used in the present invention are shown in Table 3.

TABLE 3

	M1	M5	W3WO	M3
Cementitious material	Slag	Slag/ Portland	Portland	Portland
Fineness (cm^2/gm)	13000	9000	10000	11300
Sp. Gr. (gm/cm^3)	3.00	3.00	3.06	3.06
Composition (wt%)				
SiO_2	35.4	30.6	18.93	17.90
Al_2O_3	16.0	12.4	18.93	4.93
Fe_2O_3	0.3	1.1	3.78	3.48
CaO	43.3	48.4	61.57	61.63
MgO	3.5	5.8	2.96	2.59
K_2O	0.64	0.68		
Na_2O			0.44	0.36
SO_3	0.3	0.8	4.11	5.68
L.O.I. (Loss on Ignition) 1000°C			2.40	2.90
IR (Insoluble Residue)			0.45	0.42
TOTAL	98.8	99.5	100.00	100.00

M5 is a mixture of slag and portland cement which is ground to the indicated degree of fineness after mixing. Thus, the slag and cement are co-ground. W3W is portland cement ground with a polymeric grinding aid and M3WO is portland cement ground without a grinding aid. M3W and M3WO are useful to produce slag/cement mixtures by mixing with MICROFINE slag such as M1. The result is a mixture of individually ground MICROFINE cements which therefore were not co-ground. In some cases there are advantages in using such slag/cement mixtures over co-ground mixtures. Individual grinding can be done in an optimum way for the specific slag and cement, but co-grinding tends to be an optimum procedure only for one of the components.

By means of individual grinding, a very high degree of fineness can be obtained in the mixture. Furthermore individual grinding enables production of mixtures in which the fineness of the mixture can be easily varied to suit particular needs.

High level of penetration into a tight formation associated with high permanence renders the present invention valuable in many applications. One example is radioactive waste storage in shafts deep in rock formations where the present invention may be employed to permeate the rock around the waste for secondary containment.

It is a feature of the invention that cementitious material having the fine particle size and distribution described is formulated in a composition producing high strength grout having a readily controlled set time.

While slag or slag plus cement are preferably used without inert filler material, in some instances it may be desirable to incorporate limited amounts of other solids meeting the particle size specification specified for slag herein. Such other solids are clay, bentonite, kaolin, vermiculite, limestone, silica flour, silica fume and other well known inert solids. The amount of these employed is to be minor so as not to reduce the strength of the set grout below desired values.

The dispersant is selected from materials used to disperse solids, preferably water-wetable solids, in aqueous systems. The dispersant serves to aid the penetration of water into the finely divided solids to produce a suspension of unassociated or unagglomerated particles. These dispersants are generally negatively charged or anionic electrolytes especially polyelectrolytes, such as polycarboxylates and polysulphonates. Examples include sodium ammonium salts of polymethacrylic acid, diisobutylenemaleic anhydride copolymer, copolymers of acrylic, methacrylic and maleic acids, organic phosphates, sulfonated naphthalene formaldehyde condensates, sulfonated natural products and other sulfonated polymer condensates.

The particle size of the materials is determined by a laser light scattering particles size distribution apparatus identified as a Microtrac R particles size analyzer (Leeds and Northrup Instruments, North Wales, Pa. 19454). Measurements are made in the 0.7 to 125 micrometer range and are presented in terms of the volume of particles in size channels having a size ratio of approximately 1.4 between channels. Results are given as the percent larger than the stated size for each channel limit and the calculated volume surface area of the sample in square meters per cubic centimeter. The volume surface area can be converted to the specific surface, in square meters per gram, by dividing by the density of the material. Portland cement density is considered 3.15 grams per cubic centimeter as in ANSI/ASTM standard C 104-78a; slag density is considered 2.92 grams per cubic centimeter.

Set time and settling are determined by the following general procedure:

1. the components are mixed in a plastic cup, as described in the hereinbelow Examples.

2. the mixture is colloidally agitated for 10 seconds by a high speed mixer.

3. the cup is tilted periodically while the CM surface is observed. When there is no flow or gross motion of the CM surface while the cup is tilted to 45 degrees the time is noted; this is the set time. Settling of the CM is observed; the percent of the total volume present as clear or cloudy surface liquid is reported as percent settlement.

Hardness development is monitored by measurement of the compressive strength and is reported along with the time of the measurement elapsed after sample preparation. The strength measurement employs a handheld penetrometer (Soiltest CL-700 Pocket Penetrometer*, Soiltest Inc., Chicago, Ill.) and follows the manufacturer's instructions. The penetrometer is held by its handle with the piston at right angles to the CM surface. With steady pressure the piston is pushed into the CM to the depth of the calibration groove about 1/4 inch from the end of the piston. The compressive strength is read on the scale of the instrument.

It is advantageous to utilize slag as the cementitious material rather than portland cement in the grouting method and composition of the present invention, for several reasons. First, the slag component is available commercially in very finely divided form, such as the product described above which has a specific surface area of 14,000 cm^2/g; the slag is less costly, and offers the advantage of being non-polluting. However, the hydraulic reactivity of such slag is low, and a number of the intended applications require a reasonably fast set time and hardening time, that is, attaining desired strength in a reasonable time. Furthermore, in number of the intended uses for the present method and composition, it is important to obtain a low water permeability in the grouted formation. Thus, in such uses, a low percent settlement is desired (so that all the pores and openings in the formation being grouted are filled). The grouting composition desirably should exhibit a set time of below 6 hours, but not less than 0.5 hour. Preferably the set time is from 1 to 5 hours, more preferably from 1 to 4 hours and most preferably from 1 to 2 hours.

A desirable hardening time for the present invention is obtained when the strength of the grout is at least 4.5 kg/cm^2 within 20 hours, preferably in less than 10 hours and more preferably in less than 6 hours.

The percent settlement desired depends on the intended use, and normally should be below 50% (volume).

*Trade-mark

It is more desirable for percent settlement to be below 45%, with a settlement of 0-35% being more preferable and 0-10% settlement being most preferable.

However, the particular application of the present method and composition will determine the best choice of properties. For example, in situations involving water containment such as stabilizing or containing hazardous waste, low percent settlement is desired and for this purpose the water/CM (WC) ratio may be chosen to be low in water. For uses which involve strengthening formations where water containment is not a problem, the WC may be chosen to be higher in water. A higher ratio means use of less of the CM component and therefore is less costly.

In addition to requirements imposed by the intended use, the nature of the formation must be considered. A formation having larger openings or pores to be grouted can be grouted with a composition having a low WC but a formation into which the grout can penetrate only with difficulty, even with use of high pressure pumps, may require a higher WC to lower grout viscosity.

It is an advantage of the method and composition of the invention that the grout can be formulated to have the most desirable combination of these properties for the particular intended use and nature of the formation. The components of the grout may be selected to modify the properties as desired, and modification is also possible through use of optional additives.

For uses of the method in stabilizing or strengthening formations, a low WC is needed where high strength is needed in the grouted formation. However, in such uses, the permeability of the resulting grouted formation is usually is not a problem so that a low permeability does not have to be achieved. Furthermore, many situations involving stabilization do not also call for high strength in the formation. As a result, a higher water proportion in the WC can be employed. For stabilizing and strengthening formations, it is preferred in the method and composition of the present invention to use a WC in the range of 1:1 to 10:1 by weight.

The present invention is illustrated in the drawings wherein Fig. 1 is a ternary phase diagram illustrating the relative proportions of calcium, aluminum and silicon oxides. Areas are shown representing blast furnace slag 1 with M1 MICROFINE slag 2 located therein, M5 MICROFINE slag/cement 3, portland cement 4, fly ash 5 and alumina cement 6.

Fig. 2 schematically depicts a tube-a-machette system for injection of grout into a formation, which may be employed in the method of present invention. A grout pipe 30 is installed in borehole 37. Lean cement grout 41 fills the space between grout pipe 30 and the wall of borehole 37. Grout pipe 30 has a plurality of ports 32 closed by tight-fitting rubber sleeves 33, acting as a check valve. Sleeve 33 is shown in closed position 34 and open position 35. Injection tube 31 moves double-ended packer 39 which isolates individual ports 32, permitting injection through isolated ports at specific depths. A grouting composition used in the present invention is injected through pipe 31 as shown by arrows. The grout is pumped under pressure which moves sleeve 33 away from port 32. The grout under pressure breaks through lean cement grout 41 into passage 42. In this way the grout is injected into the formation as shown by arrows, and forms a spreading grout region 40.

An alternative procedure is to drill the borehole while inserting a 3 inch steel casing during drilling. Upon completion of the borehole, the drill is removed and the steel casing remains in the borehole. The interior of the casing is filled with a lean cement grout (high water content). The above-described tube-a-machette is inserted into the casing while the lean grout is fluid, and then the casing is removed. The lean grout is allowed to harden, whereupon it seals the annular space around the tube-a-machette. The lean cement grout fractures when subjected to the impact of high pressure grout being injected through the ports of the tube-a-machette.

The method of the present application is of particular use in cementing wellbores and in grouting porous gas - and petroleum - bearing formations, i.e. formations in which hydrocarbons such as natural gas and petroleum are found. These geological formations containing hydrocarbon deposits include porous reservoir rocks, sand, shale, sandstone, and limestone. The method of the invention has advantages in well drilling and production operations, and especially for primary or remedial cementing of a wellbore, such as squeeze cementing.

Specific techniques for primary and remedial cementing are described in the above mentioned "Worldwide Cementing Practices" publication. Primary cementing involves introduction of cement into the space between the outside of the steel casing of the well and the borehole wall (or the inside of a previously set casing if a new casing was introduced). Cement slurry is pumped down the entire length of the casing, out the borehole joint and into said space. Remedial cementing concerns procedures to remedy undesired conditions in a well such as to shut off water flows or repair casing damages. The most common remedial cementing procedure is called squeeze cementing.

Squeeze cementing has been described in the above publication as being the process of applying hydraulic pressure to a cement slurry to (1) force or "squeeze" the slurry into the desired location and (2) force water from the slurry after placement to create a mass which will remain in place and harden to provide a seal. The publication lists some reasons why squeeze cementing is done, as follows:

1. Repair of a faulty or inadequate primary cement job.
2. Shut off unwanted water or gas.
3. Isolate a zone prior to perforating for production.
4. Abandon a nonproductive zone.
5. Seal off thief zones or lost circulation during drilling.
6. Repair casing leaks.
7. Modify injection profile in injection wells.
8. Provide initial seal for a liner (tack and squeeze).

It is known in the art that there are difficulties in achieving success in such cementing operations due to the difficult conditions encountered in wells. Portland cement has been used in the typical cement slurry for well cementing, but has disadvantages because of a particle size larger than pore diameters of the formation, and because of relatively short thickening or set times. The latter is a special problem in deeper wells having an increased temperature with depth, causing too rapid thickening which adversely affects pumping and placement of the cement. It is also important for the hardened cement to have sufficient strength.

MICROFINE cements used in the present method are cementitious grouting materials composed of ultrafine particles of slag and portland that exhibit excellent penetrability, strength and durability suitable for squeeze cementing of oil well matrices, especially for gas and water control.

Application of ultrafine cements in squeeze cementing is enhanced by ultrafine particle size for penetration of medium sands and finely cracked rock in oil well matrices. Filtration properties (ability to hold water) are excellent because of ultrafine particle size and addition of one percent dispersant lowers viscosity and extends initial hardening time at high temperatures in the oil well matrix.

The present method therefore is suitable for the following squeeze cementing applications:

Reduce High GOR (Gas/Oil Ratio)
Control Excess Water
Repair Casing Leaks
Seal Off Thief Zones
Protection Against Fluid Migration

The following properties of the ultrafine cement allow penetration of the oil well matrix.

(a) Penetrating Power: MICROFINE particle size (maximum 2 percent at 2 micron) allows the grout to penetrate fine sands and finely cracked rock in well matrix.

(b) High Hardened Strength: MICROFINE grains are naturally activated with portland to rapidly harden to high strength.

(c) Excellent Durability: after hardening by hydrating, the ultrafine cements acquire high impermeability which protects them from sulfates and chlorides to insure high durability.

(d) Long Initial Hardening Time: combination of ultrafine slag and portland provides long fluid time at high temperature and pressure for maximum penetration of oil well matrix.

Application of the ultrafine cements in squeeze cementing is enhanced by ultrafine particle size for penetration of medium sands and finely cracked rock in oil well matrices. Filtration properties (ability to hold water are excellent because of ultrafine particle size and addition of dispersant lowers viscosity and extends initial hardening time at high temperatures in the oil well matrix.

The MICROFINE slag/cement has excellent set time, initial hardening time and viscosity in well cementing. Longer set and hardening times at high temperature result from larger quantities of blast furnace slag in the M5 ultrafine cement. The longer initial hardening time allows for down hole cementing for deep wells. Appropriate accelerators and retarders may be used for varying well depths and temperatures.

The following oil well squeeze cementing operations (besides others) may be performed with M5 MICROFINE cement:

Abandonment

Fine sands and finely cracked rock around non-commercial well zones may be sealed with M5. A prudent practice in abandoning a set of perforations is to set a drillable squeeze packer and attempts to squeeze the abandoned perforations with a low fluid loss cement at less than fracturing pressure.

Block Squeeze

Block squeeze is used before perforating for production to prevent fluid migration from either above or below. M5 will penetrate blocked matrix better than ordinary portland to more efficiently prevent fluid migration.

Squeeze Unwanted Water

Water is an integral part of all porous rock and is present in most oil and gas bearing formations. Migration of water may be controlled when larger quantities of low viscosity M5 slurry penetrate the matrix pore spaces at less than fracturing pressure.

Reducing GOR (Gas Oil Ratios)

During the life of a well the GOR may increase beyond the economic limit, necessitating remedial action. A common procedure is to squeeze off all the perforations in the oil and gas zones which may be done with M5 and then perforate at selected intervals.

Thief Zones

M5 may be used to seal off thief zones in the upper section of a slotted gravel pack liner. Using a combination of M5 and microflour, a thief zone may be sealed to increase production.

The ultrafine cements have been found to be significant additions to cementitious materials for oil well cementing because of the following inherent properties:

1. Ultrafine particle size allows penetration of fine sands and finely cracked rock in the oil well matrix.

2. Inherent long initial hardening time because of high ultrafine slag content may be enhanced with polymer accelerators and retarders.

3. Low clear settlement, non hard settlement and medium viscosity from ultrafine particle size may be improved with viscosity reducers and dispersants.

4. Inherent low slurry density and high hardened strength from high ultrafine slag content allows penetration of microchannels caused by gas migration.

Fundamental ultrafine particle size, long initial hardening time and high hardened strength of the ultrafine cements may be enhanced by the use of modern polymer technology accelerators, retarders, dispersants and fluid loss polymers. Physical properties of the ultrafine cement may also be improved by the addition of silica fume, bentonite, sodium silicate and silica flour.

As mentioned above, M5 cement is available in the desired particle size. In some applications it will be advantageous to further grind all or part of the cement/slag, especially in the field, i.e. in locations near the formation to be grouted.

The portland cement component may be further ground prior to mixing with slag by grinding particulate portland cement having a particle size wherein less than 10 wt. percent of the particles are larger than 10 micrometers in diameter to a particle size wherein less than 2 wt. percent of the particles are larger than 10 micrometers in diameter, in a tower mill at or near the location of said formation to be grouted.

Also, particulate slag and particulate portland cement may be co-ground to a particulate size wherein less than 2 wt. percent of the particles are larger than 10 micrometers in diameter in a tower mill at or near the location of said formation to be grouted.

Mixtures of 75% MICROFINE slag and 25% MICROFINE portland are especially useful in oil well cementing and can be produced by such tower mill grinding.

Apparatus and techniques for Tower mill grinding are known. Typically dry and wet Tower Mills are approximately 10 feet high and 2 feet diameter, charged with 1/2" stainless steel or ceramic balls, all internally rubber lined with a screw rotating at 35-85 rmp.

The following examples are included to illustrate the invention.

Definitions of symbols used in the examples:

W	Water
CM	Cementitious material
M1	Slag ground to 14,000 cm^2 SSA
M3W	MICROFINE portland cement ground with a polymer grinding aid to 11,300 cm^2/g SSA
M3WO	MICROFINE portland cement ground without a grinding aid to 10,000 cm^2/g SSA
M5	MICROFINE portland/slag co-ground to 8,880 cm^2/g SSA
C6	Dispersant, 3000 MW polyacrylic acid copolymer
N2	Dispersant, naphthalene sulfonate formaldehyde condensate
FL	Accelerator, a 50% aqueous solution of calcium nitrate (Sika Corp., Lyndhurst, N.J.)
HE	Accelerator, a 30% aqueous solution of calcium chloride (Sika Corp., Lyndhurst, N.J.)
D	Dispersant
DCI	Corrosion inhibitor, a 30% aqueous sodium nitrate solution (W. R. Grace Co.)
4180	Dispersant, a copolymer of acrylic acid
M	MICROFINE slag, slag/cement or portland cement
WC	Weight ratio of water to cementitious material
A	Accelerator
LiS	Accelerator, lithium sodium polysilicate, available from Lithium Corporation of America, (lithsil S), a typical analysis of this product being: Li_2O (1.8) Na_2O (1.2) SiO_2 (19.6), 22.6% solids
Li6	Accelerator, lithium polysilicate, available from Lithium Corporation of America, (lithsil 6), a typical analysis of this product being: Li_2O (2.2) SiO_2 (20.7), 22.9% solids

Example 1 gives data on the properties of grout injected by the method of the invention. Neat grout is the grout in absence of sand, such as when injected into a rock formation.

EXAMPLE 1

Material Tested

Ottowa 20-30 sand	U.S. Silica Company, IL
MC-100 MICROFINE cement (M1)	Blue Circle Atlantic Baltimore, MD
MC-500 MICROFINE cement (M5)	Onoda Cement, Tokyo, Japan
Ordinary Portland	(OP) Chicago, IL
M3WO MICROFINE portland (223)	Heracles Cement, Athens, Greece
M3W MICROFINE portland (224)	Heracles Cement, Athens, Greece

Particles Size and Composition

TABLE 4

Particle Size Distribution of Ottowa 20-30 Sand, M1, M5, OP

	Grain Size (mm)			
	20-30 Sand	M1	M5	OP
Percent Finer (wt)				
100	0.840	0.0070	0.0100	0.070
80	0.550	0.0040	0.0057	0.027
60	0.520	0.0026	0.0037	0.017
40	0.500	0.0017	0.0023	0.008
20	0.480	0.0010	0.0014	0.003
0	0.420	0.0007	0.0008	0.009

Neat Sample Preparation

1. Add 5 grams of N2 to 500 grams of water and mix.

2. Add 500 grams of M5, shake and disperse in Hamilton Beach high speed mixer for one minute.

3. Pour mix into pre-slit PVC pipe, one inch ID by one foot long.

4. After desired curing time, open slits, remove sample and cut in 2 inch lengths, trim and smooth end faces.

Grout Injection Mold Preparation

1. Use ASTM Standard D4320-84 for grout injection mold set up.

2. Use three piece split mold, 38 mm ID by 96 mm long segmented 120 degrees each, rubber gasket and glued along segments.

3. Three hose clamps are spaced equally along cylinders to compress gaskets.

4. End of cylinders are seated with round rubber gaskets, placed in end plates ready for filling with sand.

5. To allow easy flow of grout without moving sand particles, place perforated plastic disc and filter mesh in bottom of mold.

6. Air dried 20-30 Ottowa Sand is poured into mold in three equal layers compressed at each layer with a 320 gram cylinder.

7. Using a hand-held Burgess Vibrotool*, each layer of sand is vibrated for one minute until cylinder is filled.

8. A filter mesh (70 mesh polyester screen) and a perforated disc (12-1/16th inch diameter holes) and rubber gasket are placed on the sand. End plate is secured by tightening tie bolts.

9. Samples prepared by this procedure give consistant results in void ratio (average 0.52) and relative density at this void ratio is 80%.

Grout Injection Procedure

1. Samples are wetted by injection water through sample bottom at 1 psi for one minute and soaked for 15 minutes.

2. One liter batches of M5 were prepared with one percent N2 on M5 and 1:1 WC ratio. Batch mixed in a Waring Blender* for one minute before transferring to a two liter pressure tank.

3. Grout injection set up consists of six sample cylinders, holding tank

*Trade-mark

and pressure regulator.

4. Grout flow is started by placing 2 psi air in holding tank. Grout flow is stopped when 200 ml is passed through each sand cylinder. Samples are held in molds for three days curing.

Unconfined Compression Test

1. Use ASTM Standard D4129 for testing M5 with strain rate of 0.2 mm/min.

2. Unconfined compressive strength of neat M5 in 3, 7 and 28 days is outlined in Table 5.

3. Effect of curing time on strength of neat M5 and OP is shown in Table 6.

4. Effect of curing time on strength of M5 grouted sand at various WC ratios is shown on Table 7.

TABLE 5

Stress Strain Data for Neat Grout

M5 (WC 1:1, 1% N2 on M5)

Strain Rate 0.2 mm/min

	3 day	7 day	28 day
Strength (kg/cm^2)	68	163	234
Strain (%)	1.30	1.05	0.95

TABLE 6

Effect of Curing Time on Strength of Neat M5 and OP

M5 (WC 1:1, 1% N2 on M5)

Strain Rate 0.2 mm/min

	3 day	7 day	28 day	60 day
Strength (kg/cm^2)				
M5	57	170	240	290
OP	80	133	190	210

TABLE 7

Effect of Curing Time on Strength of Grouted Sands

M5 (WC 1:1, 2:1, 3:1, 1% N2 on M5)

Strain Rate 0.2 mm/min

	7 day	14 day	28 day	60 day
Strength (kg/cm^2)				
M5 (WC 1:1)	110	128	162	202
M5 (WC 2:1)	27	36	49	63
M5 (WC 3:1)	8	13	18	24

Creep Test Procedure

1. Creep test of M5 grouted sand was performed using standard procedures on creep testing equipment.
2. Percent Strain verses time of M5 grouted sand is shown in Table 8.

TABLE 8

Creep of M5 Grouted Sand

Strain (%)

Days	0	20	40	60	80	100	120	140	160
D=0.7	.1	.19	.20	.22	.25	.26	.27	.28	.29
D=0.8	.65	.68	.70	.72	.73	.74			

D= Percent of failure load of M5 grouted sand

Permeability Test Procedure

1. Permeability of M5 grouted sand was performed using standard procedures with triaxial permeability cells.
2. Effect of curing time on permeability of M5 grouted sand at 1:1 and 3:1 WC ratio is shown in Table 9.

TABLE 9

Effect of Curing Time on Permeability of Grouted Sand

M5 (WC 1:1 and 3:1, 1% N2 on M5)

Permeability (cm/sec)

	4 day	7 day	20 day
WC 3:1	10^{-5}	$10^{-5.1}$	$10^{-5.2}$
WC 1:1	$10^{-7.2}$	$10^{-7.4}$	$10^{-7.5}$

In the following examples, a gray color indicates that the cement is not fully hard, a blue color shows that it is fully hard, and numerical values for compressive strength are expressed in kg/cm^2.

EXAMPLE 2

Experiment 60 was performed to determine set time, initial hardening time, compressive strength, clear and hard settlement for M5 MICROFINE cement and Type III Portland at 20, 40, 60 and 90°C.

Formulation

	60A grams	60B grams
Water	100	100
N2	1	1
M5	100	-
Type III Portland	-	100

Run 60A: M5 MICROFINE Cement

Viscosity at 0 hr: 15 cps (10 rpm, UL Adapter Brookfield); at 1 hr: 100 + cps

at 20°C, Hours:	0	1	2	3	4	5	7	8	20
% Clear Settlement	0	0	5	10	10	15	20	20	20
% Hard Settlement		0	0	0	0	0	0	0	0
Set Time	f[1]	f	f	f	f	f	f	f	set
IHTS [3]	s[2]	s	s	s	s	s	s	s	2

at 40°C, Hours:	0	1	2	3	4	5	7	8
% Clear Settlement	0	5	10	15	15	15	15	15
% Hard Settlement	0	0	0	0				
Set Time	f	f	f	f	set			
IHTS	s	s	s	s	s	4	<4.5	

at 60°C Hours:	0	1	2	3	4	5	7	8
% Clear Settlement	0	10	10	10	10	10	10	10
% Hard Settlement	0	0	0					
Set Time	f	f	f	set				
IHTS	s	s	s	s	s	0.25	b(b)	>4.5

at 90°C Hours:	0	1	2	3	4	5	7	8
% Clear Settlement	0	10	10	10	10	5	5	0
% Hard Settlement	0							
Set Time	f	f	set					
IHTS	s	s	s	s	0.1	b	<4.5	

60B: Type III Portland (Whitehall, LaFarge)

Viscosity at 0 hr: 10 cps (10 rpm, UL Adapter Brookfield); at 1 hr: 70 cps

at 20°C Hours:	0	1	2	3	4	5	7	8
% Clear Settlement	10	10	20	20	20	20	20	20
% Hard Settlement	0	80	80	80				
Set Time	f	f	f	f	set	g(5)		
IHTS	s	s	s	s	s	0.1	4.00	>4.5

at 40°C Hours:	0	1	2	3	4	5	7	8
% Clear Settlement	0	20	30	30	30	30	30	30
% Hard Settlement	0	70	80	80				
Set Time	f	f	f	f	set	g		
IHTS	s	s	s	s	s	0.1	<4.5	

at 60°C Hours:	0	1	2	3	4	5	7	8
% Clear Settlement	0	20	30	30	30	30	30	25
% Hard Settlement	0	70	80					
Set Time	f	f	set	g				
IHTS	s	s	s	s	>4.5			

at 90°C Hours:	0	1	2	3	4	5	7	8
% Clear Settlement	0	30	25	20	20	20	10	10
% Hard Settlement	0	70						
Set Time	f	f	set		g(5)			
IHTS	s	s		1	<4.5			

(1) fluid
(2) soft
(3) initial hardening time and strength (kg/cm^2)
(4) blue
(5) gray

EXAMPLE 3

Experiment 61 was performed to determine viscosity, clear settlement, set time, initial hardening time and compressive strength for M3 portland and M1 slag at 20, 40, 60 and 90°C.

Formulation

	61A grams	61B grams
Water	100	100
N2	1	1
M3	100	25
M1	-	75

61A: M3 MICROFINE cement

Viscosity at 0 hr: 100 cps (10 rpm, UL Adapter, Brookfield); at 15 min; 100 + cps

at 20°C, Hours:	0	1	2	3	4	5	6	7	8
% Settlement	0	5	5	10	10	10	5	5	0
Set Time	f[1]	set							
IHTS [3]	s[2]	s	s	s	s	s	0.1	3	>4.5

at 40°C, Hours:	0	1	2	3	4	5	6	7	8
% Settlement	0	0	0	0	0	0	0	0	0
Set Time	f set [4]								
IHTS	s	s	0.5	3.5	>4.5				

at 60°C, Hours:	0	1	2	3	4	5	6	7	8
% Settlement	0	0	0	0	0	0	0	0	0
Set Time	f set [5]								
IHTS	s	0.1	>4.5						

at 90°C, Hours:	0	1	2	3	4	5	6	7	8
% Settlement	0	0	0	0	0	0	0	0	0
Set Time	f set [6]								
IHTS	s	0.5	>4.5						

61B: 75% M1/25% M3

Viscosity at 0 hr: 100 cps (10 rpm, UL Adapter, Brookfield)

at 20°C, Hours:	0	1	2	3	4	5	6	7	8	9	17
% Settlement	0	5	5	5	5	10	10	10	5	0	0
Set Time	f	f	set								
IHTS	s	s	s	s	s	s	s	s	s	0.1	4.0

at 40°C, Hours:	0	1	2	3	4	5	6	7	8	9	17
% Settlement	0	5	5	5	5	5	10	10	5		
Set Time	f	set									
IHTS	s	s	s	s	s	s	s	s	0.1	2	>4.5

at 60°C, Hours:	0	1	2	3	4	5	6	7	8
% Settlement	0	5	5	5	5	0	0	0	0
Set Time	f set (4)								
IHTS	s	s	s	s	s	0.1	2	>4.5	

at 90°C, Hours:	0	1	2	3	4	5	6	7	8
% Settlement	0	30	25	20	20	20	10	10	10
Set Time	f set (6)								
IHTS	s	s	s	0.1	>4.5				

(1) fluid
(2) soft
(3) initial hardening time and strength (kg/cm^2)
(4) 40 minutes
(5) 30 minutes
(6) 20 minutes

EXAMPLE 4

An experiment 62 was performed which demonstrates a low density slurry and high compressive strength of the cement for 1:1 water cement ratio M5 (61A) compared with Type III portland (62A) as follows:

Formulation

	62A (grams)	62B (grams)
Water	100	100
NS-200 Dispersant	1	1
M5	100	-
Type III Portland	-	100
	201	201

Density M5 Slurry

Slurry	266 grams
Tare	119
	147 gm/100 ml x 8.34 = 12.3 lbs/gal

Density Type III Portland

Slurry	271 grams
Tare	119
	152 gm/100 ml x 8.34 = 12.7 lbs/gal

Compressive strength of 1:1 WC M5 is 4500 psi at 20°C compared with 2300 psi for other light weight blends at 27°C. This indicates that M5 MICROFINE cement has inherent properties for oil-well cementing when the combination of light weight slurry and high compressive strength is required.

EXAMPLE 5

In Experiment 63, the properties determined were viscosity, set time, initial hardening time and strength of M5 at 1:1, 0.9:1, 0.8:1, 0.7:1 and 0.5:1 water cement ratios at 20, 60, 70 and 80°C.

Formulation

	63A (g)	63B (g)	63C (g)	63D (g)	63E (g)
Water	100	90	80	70	50
N2	1	0	1	2*	2
MC-500	100	100	100	100	100
WC Ratio	1:1	0.9:1	0.8:1	0.7:1	0.5:1

* 1g initially, and subsequent additional 1g

Viscosity

	Minutes	Visc (20°C) (cps)	Visc (60°C) (cps)	Comments
63A	0	5		
	5	10		
	7		70	
	10		100	
63B	0	6		
	5	8		
	10		15	
	15		40	
	20		100	
63C	0	11		
	5		25	
	10		65	
	12		100	
63D	0		100	1% N2 (based on Cement), Additional 1% N2 added, 20°C Heated 80°C outside water Measured 60°C inside
	5		20	
	6		3	
	8		2	
viscometer				
	10		3	" " " "
	20		5	" " " "
	25		5	" " " "
63E	0		100	2% N2 added, 20°C Heated 85°C outside water Measured 70°C inside
	1		45	
	2		10	
viscometer				
	5		12	" " " "
	7		15	Measured 60°C inside
viscometer				
	10		20	" " " "
	15		25	" " " "
	20		25	" " " "
	25		3	" " " "

SET & INITIAL HARDENING TIME AND COMPRESSIVE STRENGTH (kg/cm^2)

	Hours										
	0	1	2	3	8	10	11	12	20	44	88
	20°C				80°C			20°C			
A.	f(1)	f	set	s(2)	s	s	0.1(3)	0.5	2.0	>4.5	b(4)
B.	f	f	set	s	s	s	s	0.1	0.1	>4.5	b
C.	f	f	set	s	s	s	s	0.1	0.5	>4.5	b
D.	f	f	f	set	s	s	0.1	0.5	1.0	2.0	3.0
E.	f	f	f	set	s	0.5	1.5	3.5	>4.5	g(5)	

(1) f = fluid

(2) s = soft

(3) kg/cm^2

(4) b = blue

(5) g = gray

CLAIMS:

1. A method of grouting a porous gas - and petroleum - bearing formation, which comprises injecting into the formation or into a wellbore formed in the formation, a composition comprising:

(a) water,

(b) particulate slag having a specific surface area greater than about 9,500 cm^2/g with less than 3 wt. percent of the particles of the slag being larger than 7.8 micrometers in diameter, the water and the slag being in such proportions that a water to slag weight ratio is between 0.3:1 and 10:1;

(c) at least one dispersant in an amount effective to disperse the particles of the particulate slag; and

(d) an accelerator in an amount effective to provide hydraulic reactivity to the slag.

2. The method according to claim 1, which comprises injecting the composition for primary or remedial cementing of the wellbore.

3. The method according to claim 1, wherein the particulate slag additionally has mixed with it particulate portland cement having such a particle size that less than 2 wt. percent of the particles of the portland cement are larger than 10 micrometers in diameter, the slag being at least 40 percent by weight of the total of the portland cement and the slag, and the portland cement activates hydration of the slag and partly or fully replaces the accelerator (d).

4. A method according to claim 3, which comprises one or more of:

(a) a naphthalene sulfonate formaldehyde condensate as the dispersant, in an amount of up to 2 percent by weight based on the total weight of the slag and the portland cement to decrease viscosity and retard set time;

(b) silica flour added in a proportion wherein the silica flour is not more than 50% of the total weight of the silica flour, the slag and the portland cement; and

(c) a retarder other than the naphthalene sulfonate formaldehyde condensate, added in an amount effective to obtain desired longer set and hardening times.

5. A method according to claim 1 or 2, which comprises one or more of:

(a) a naphthalene sulfonate formaldehyde condensate as the dispersant, in an amount of up to 2 percent by weight based on the slag to decrease viscosity and retard set time;

(b) silica flour added in a proportion wherein the silica flour is not more than 50% of the total weight of the silica flour and the slag; and

(c) a retarder other than the naphthalene sulfonate formaldehyde condensate, added in an amount effective to obtain desired longer set and hardening times.

6. The method according to claim 1, 2 or 5, wherein the proportion of the slag is such that the water to slag ratio is 0.5:1 to 2:1.

7. The method according to claim 3 or 4, wherein the particles of the portland cement have a specific surface area greater than 6,000 cm^2/g with less than 16% by weight of the particles being larger than 7.8 micrometers in diameter.

8. The method according to claim 3 or 4, wherein the particles of the portland cement have a specific surface area greater than 10,000 cm^2/g with less than 3% by weight of the particles being larger than 7.8 micrometers in diameter.

9. The method according to claim 1, 2 or 3, wherein the dispersant is at least one anionic electrolyte selected from the group consisting of polycarboxylates and polysulfonates.

10. The method according to claim 1, 2, 3 or 9, wherein the accelerator is at least one member selected from the group consisting of alkali and alkaline earth oxides, hydroxides and salts.

11. The method according to claim 10, wherein the accelerator comprises NaOH alone or in combination with Na_2CO_3.

12. The method according to claim 3 or 4, wherein the portland cement partly replaces the accelerator (d).

13. The method according to claim 3 or 4, wherein the portland cement fully replaces the accelerator (d).

14. The method according to any one of claims 1 to 13, wherein the slag has a specific surface area greater than 11,000 cm^2/g.

15. The method according to any one of claims 1 to 13, wherein the slag has a specific surface area greater than 13,000 cm^2/g.

16. The method according to any one of claims 1 to 15, wherein less than 1.5 wt. % of the particles of the slag are larger than 7.8 micrometers in diameter.

17. The method according to any one of claims 1 to 16, wherein the slag on a dry basis has the following composition (in wt. %):

SiO_2	: 30-40
Al_2O_3	: 8-18
CaO	: 35-50
MgO	: 0-15
FeO	: 0-1
S	: 0-2
Mn_2O_3	: 0-2.

18. A grouting composition for grouting a porous gas - and petroleum - bearing formation or a wellbore formed in the formation, which composition comprises:

(a) water;

(b) a particulate slag which is a ultrafine slag having a specific surface area greater than about 10,000 cm^2/g with less than 3 wt. percent of the particles of the slag being larger than 7.8 micrometers in diameter, the water and slag being in such proportions that a water to slag weight ratio is between 0.5:1 and 2:1;

(c) at least one dispersant in an amount effective to disperse the particles of the particulate slag; and

(d) an accelerator in an amount effective to provide hydraulic reactivity to the slag.

19. The composition according to claim 18, wherein the slag additionally has mixed with it ultrafine cement particles having a specific surface area greater than about 10,000 cm^2/g with less than about 7 weight percent of particles of the cement being larger than 7.8 micrometers in diameter, the slag being at least 40% of the total weight of the slag and the cement.

20. The composition according to claim 19, wherein the cement is portland cement.

21. The composition according to any one of claims 18 to 20, wherein the slag has a specific surface area greater than about 13,000 cm^2/g.

22. The composition according to claim 19 or 20, wherein the slag has a specific surface area of at least about 14,000 cm^2/g.

23. A method of grouting a porous gas - and petroleum - bearing formation, which comprises injecting into the formation a composition comprising:

(a) water;

(b) particulate slag having a specific surface area greater than about 11,000 cm^2/g, with less than 1.5 wt. percent of the particles of the slag being larger than 7.8 micrometers in diameter the water and the slag being in such proportions that a water to slag weight ratio is between 0.3:1 and 10:1;

(c) at least one dispersant in an amount effective to disperse the particles of the particulate slag; and

(d) an accelerator in an amount effective to provide hydraulic reactivity to the slag.

24. The method according to claim 23, wherein the slag has a specific surface area greater than about 13,000 cm^2/g.

25. The method according to claim 23 or 24, wherein the water to slag weight ratio is in the range between 0.5:1 and 2:1.

26. The method according to any one of claims 1 to 17 or any one of claims 23 to 25, wherein the composition is injected using a tube-a-machette system.

27. The method according to claim 3, 4, 7, 8, 12 or 13, wherein the slag is at least about 75 percent by weight of the total of the portland cement and the slag.

28. The composition according to claim 19 or 20, wherein the slag is at least about 75 percent by weight of the total of the slag and the cement.

SMART & BIGGAR
OTTAWA, CANADA

PATENT AGENTS

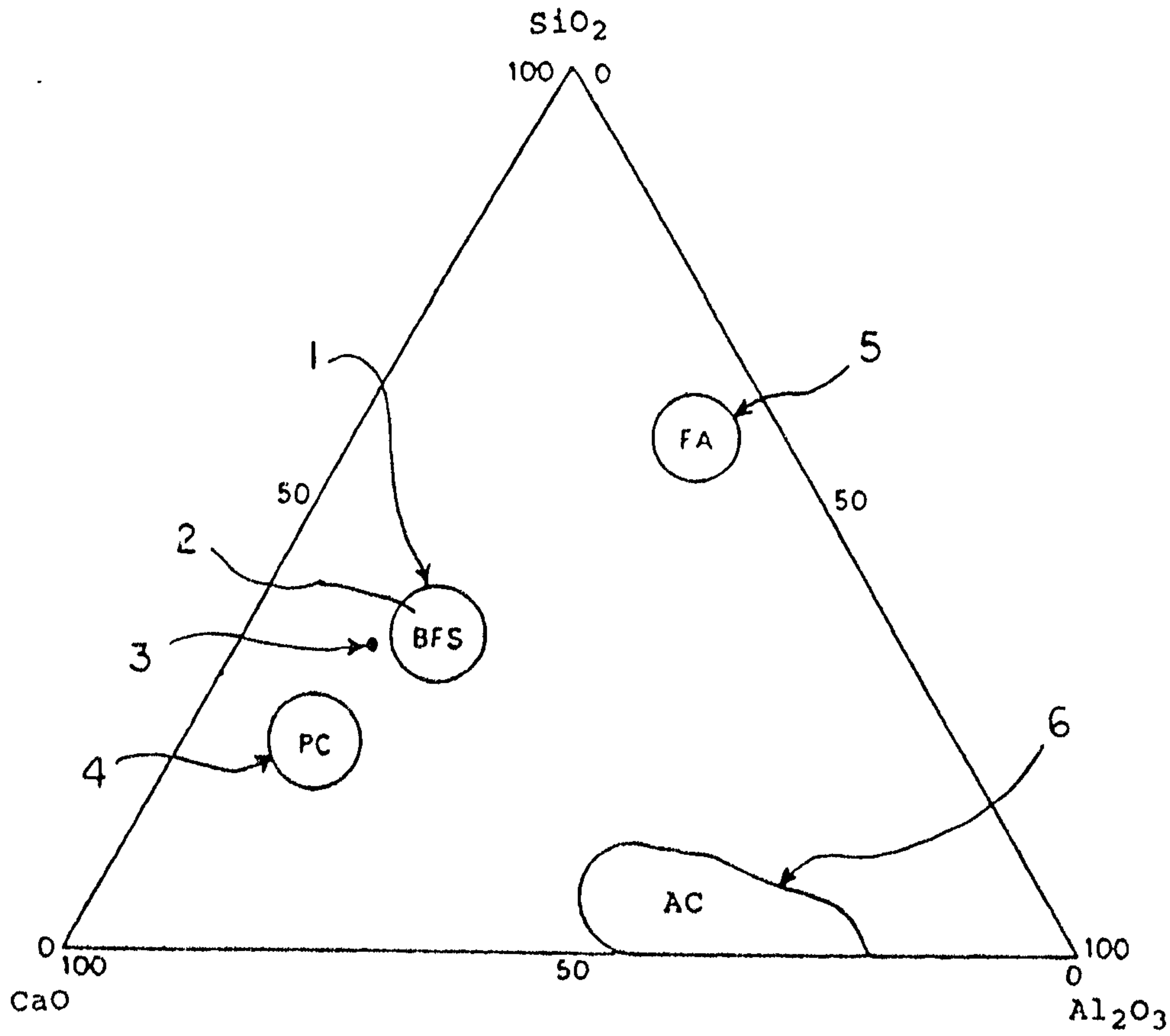

FIG. 1

2072064

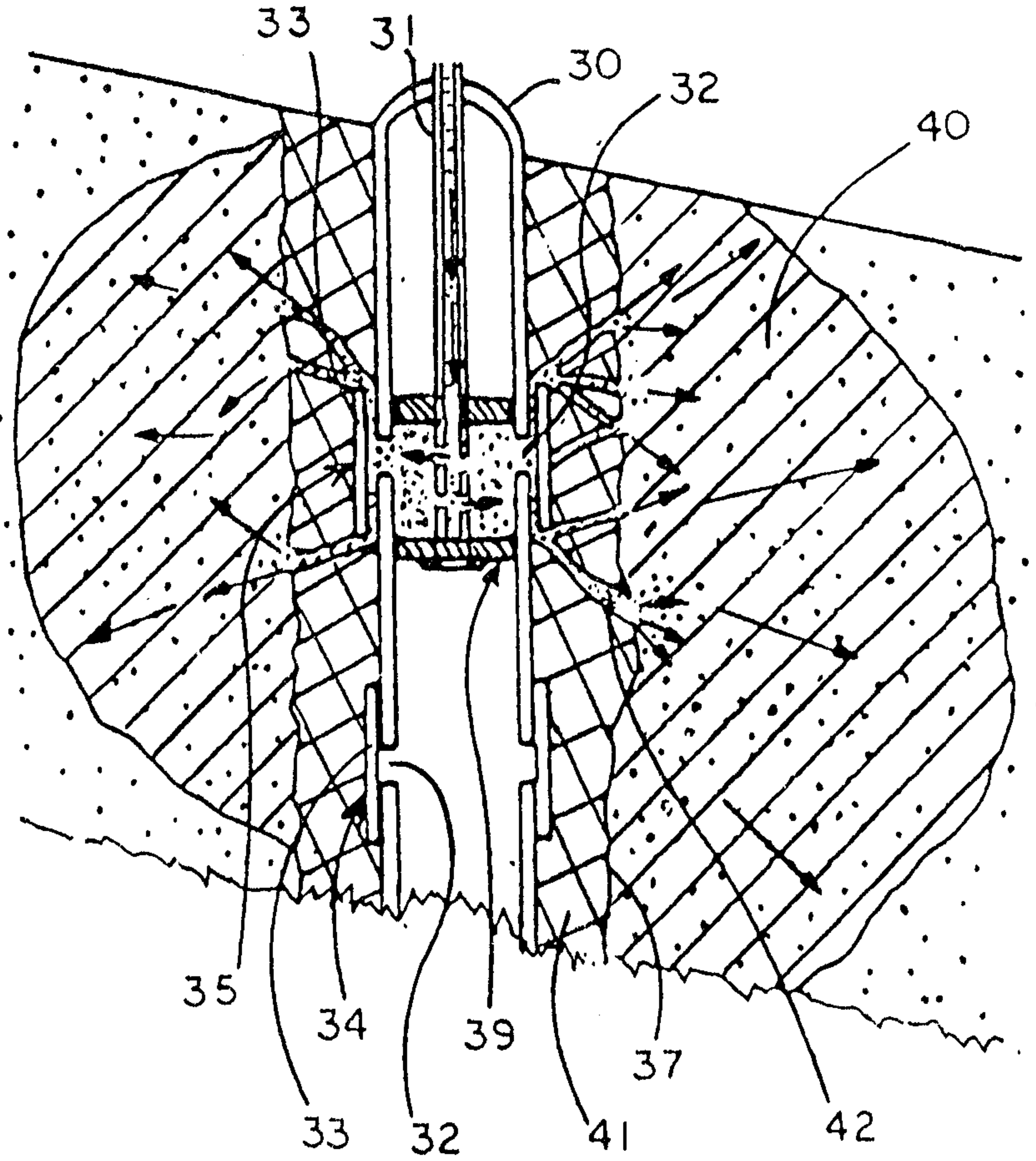

FIG. 2

R. A. Mitchell [signature]