

Description

This invention relates to a method of cementing a cylinder in a bore, particularly but not exclusively in a well bore.

During the construction of a well it is known to place a volume of a water slurry of a hydraulic cement into the annular space between the walls of the borehole and the exterior of a cylinder, or casing, wherein the cement is permitted to solidify to thereby form an annular sheath of hardened cement. The objective of the sheath, the construction of which is referred to as primary cementing, includes physical support and positioning of the casing in the borehole and prevention of unwanted fluid (liquid and gas) migration between various formations penetrated by the wellbore. The casing may for example be a conductor pipe, surface casing or an intermediate or production string. This procedure is generally known as primary cementing.

A problem encountered during primary cementing is centered upon the weight (that is the density) of the slurry itself. In certain circumstances the hydrostatic pressure developed by a column of slurry overcomes the resistance offered by a formation in which case the formation fractures or otherwise breaks down with the result that a portion of the slurry enters the formation and the desired sheath is not formed. The formation breakdown thus occurs prior in time to development of sufficient rigidity or hardening of the cement to enable it to be self-supporting.

One solution has been to reduce the density of the slurry so that the pressure developed by the required slurry height will not exceed the ability of the formation to resist breakdown. This expedient can result in sheaths having physical deficiencies such as reduced strength or increased permeability or both. Another solution has been to reduce the weight of the slurry while maintaining density by reducing the quantity of slurry pumped in a single lift or stage to thus reduce the height of slurry. This expedient requires several separate stages in order to produce the required sheath length. Time must pass between stages in order to permit previous stages to develop strength sufficient to support the weight of succeeding stages. The time expended waiting on cement to set is lost time in the process of constructing the well.

The unwanted movement of water from cracks and fractures in the formation outside of the well borehole itself may also be prevented by use of the hydraulic cement composition of this invention.

We have now found that these problems can be mitigated or overcome by using a particular hydraulic cement slurry. According to the present invention, there is provided a method of fixing a cylinder in the interior of a bore, wherein said cylinder is situated in said interior of said bore so as to define a space between the exterior of said cylinder and the wall of said bore, said method comprising the steps of introducing into said space a volume of a slurry of a hydraulic cement; maintaining said volume of said slurry in said space for a time sufficient to enable said slurry to form a sheath of rigid cement in said space to thereby fix said cylinder in said interior of said bore; characterized in that the said slurry comprises a mixture of water and hydraulic cement in the weight ratio of 0.5:1 to 5.0:1, the particle size of the cement being no greater than 17 microns, and the Blaine Fineness of the cement being no less than 7000 cm^2/g , and wherein 90% of the particles have a diameter not greater than 10 microns, 50% of said particles have a diameter not greater than 6 microns and 20% of said particles have a diameter not greater than 3 microns.

Preferably, the discrete particles of cementitious materials have diameters no larger than about 17 microns, and still more preferably no larger than about 11 microns. The distribution of the various sized particles within the cementitious material, i.e. the particle size distribution, is preferably such that 90% of them have a diameter not greater than about 10 microns and still more preferably about 7 microns, 50% have a diameter not greater than about 6 microns and still more preferably about 4 microns, and 20% of the particles have a diameter not greater than about 3 microns and still more preferably about 2 microns.

The particle size of hydraulic cement can also be indirectly expressed in terms of the surface area per unit weight of a given sample of material. This value, sometimes referred to as Blaine Fineness or as specific surface area, can be expressed in the units square centimeters per gram (cm^2/g), and is an indication of the ability of a cementitious material to chemically interact with other materials. Reactivity is believed to increase with increase in Blaine Fineness. The Blaine Fineness of the hydraulic cement used in the cementing methods of this invention is no less than about 6000 cm^2/g . The value is preferably greater than about 7000, more preferably about 10,000, and still more preferably greater than about 13,000 cm^2/g .

Cementitious materials of particle size and fineness as set out above are disclosed in various prior U.S. Patents including U.S. 4,761,183 to Clark, which is drawn to slag, as defined herein, and mixtures thereof with Portland cement, and U.S. 4,160,674 to Sawyer, which is drawn to Portland cement. The cementitious materials preferred for use in this invention are Portland cement and combinations thereof with slag wherein the quantity of Portland cement included in any mixture of Portland cement and slag used in the methods of this invention can be as low as 10 percent but is preferably no less than about 40 percent, more

preferably about 60 percent, still more preferably about 80 percent and most preferably no less than about 100% Portland cement by weight of mixture.

The material when slurried in water should exhibit a sufficiently low slurry density to enable use in situations requiring a light-weight cement which nevertheless develops satisfactory high compressive strength. In this regard the large surface area of the cement of this invention, i.e. the Blaine Fineness, renders it more reactive than cements of lower Blaine Fineness; accordingly, quantities of water greater than quantities usually employed in well cementing operations may be employed to thereby enable the formulation of slurries of low density and low viscosity without unsatisfactory loss in strength.

Thus, slurries useful herein can be formulated utilizing ratios of the weight of water per unit weight of cementitious material in the range of from about 0.5 to about 5.0, preferably from about 1.0 to about 1.75 and still more preferably from about 1.00 to about 1.5. Water to cement ratios in excess of about 1.75 and up to about 5.0 can be formulated for highly specialized applications requiring slurries of very low density and very low viscosity. It is noted, however, that slurries having such high water ratios tend to exhibit free water separation and excessive solids settling. Additives can be utilized to control free water separation and solids settling.

The slurry densities of the fine, i.e. low particle size, cements of this invention are lower than cements having usual particle sizes because of the high water ratios required to wet all of the surface area of the fine cement. The compressive strengths, however, of the set lower density slurries are satisfactory for primary cementing purposes, especially in view of the greater reactivity of the fine cements.

Considering the range of water-to-cement ratios disclosed above the slurries which can be formulated utilizing the fine cement of this invention is in the range from about 9.4 to 14.9, pounds per gallon of slurry (1.13 to 1.78 kg/l) and most preferably in the range of from about 11.5 to 12.5 pounds per gallon of slurry (1.38 to 1.50 kg/l).

One particular advantage, in addition to the low slurry densities available herein, is that the high water ratios produce low heats of hydration. Thus, the fine particle size hydraulic cement of this invention is quite useful when conducting cementing operations, and particularly primary cementing operations, adjacent to structures which may undergo undesired physical breakdown in the presence of produced heat. Examples of such structures include permafrost and gas hydrate zones.

Still another particular advantage accruing from using the fine particle size Portland cement of this invention is the observed unexpected expansion of the cement during setting. This expansion property can help prevent the formation of microannuli when the cement is used in primary cementing operations.

It is believed that this desirable expansive feature of the fine particle size Portland cement is due to the chemical content thereof and particularly to the high concentration of crystalline tricalcium aluminate (C_3A) and sulfates present therein. See, for example, Table VII. It is thought that a Portland cement having a maximum particle size of about 11 microns, a Blaine Fineness of preferably greater than about 10,000 $cm^2/gram$, a C_3A crystalline content of preferably about 3.0% or more and a sulfate content of preferably about 1.0% or more will exhibit expansive characteristics desirable in an oil field cement.

Slurries of water and the fine particle size cement of this invention are very useful to penetrate, fill and harden in fine holes, cracks and spaces such as might be expected to be found in subterranean formations in the vicinity of a well bore. By way of example, it is believed that such slurries are useful to penetrate subterranean formations having effective permeabilities as low as about 3000 to about 5000 millidarcies.

With regard to the above uses - but without being bound by the following slurry design aid - it is considered for commercial design purposes that a particle of given size in a suitable slurry as described herein can penetrate, fill and set in a crack, hole or void having a size of approximately 5 times greater than the size of the particle. Thus the 0.05 millimeter (50 micron) crack referred to above can be penetrated by a slurry of particles having a size of about 10 microns which is within the scope of the cement of this invention.

It was mentioned previously that the rate of hardening of the fine cement of this invention is related to the Blaine Fineness wherein the hardening rate increases as Blaine Fineness increases. In addition, the hardening rate is also related to the specific cementitious material being used and the temperature of the environment wherein the hardening reaction is proceeding. Thus fine particle size Portland cement, as hereinafter defined, hardens more rapidly in low temperature environments in the range of from about 30°F to about 100°F than does fine particle size slag cement, also as hereinafter defined. Also Portland cement hardens more rapidly at elevated temperatures than does slag cement.

Accordingly, to adjust to specific environments, specific slurries of fine cement can include mixtures of Portland cement and slag consistent with the concentrations previously disclosed. In general, longer set times can be achieved by increasing slag content with accompanying decrease in compressive strength and/or increasing slurry density or both.

In addition the usual well cementing additives can be combined with the cementitious materials of this invention to achieve the usual results. For example, to assist in the dispersion of individual cementitious particles in a slurry and thus to help prevent the formation of large particles by agglomeration or lumping a dispersing agent may be added to a water slurry of the cement of this invention in an amount effective to produce adequate dispersion. Such an effective amount is considered to include amounts up to about 1.5 parts by weight dispersant per 100 parts by weight of cementitious material. One such dispersant is identified by the name CFR-3 and another by the name Halad-322 each of which is disclosed and claimed in U.S. Patent 4,557,763 to George, et al., the disclosure of which is incorporated herein by reference. In view of a principle object of this invention to provide a slurry of particles which will enter very small openings and still develop adequate compressive strength the use of a material to help assure particle dispersion is considered to be an important aspect of the invention.

Other additives commonly used in well cementing which may be utilized herein include defoaming agents, fluid loss additives, lost circulation additives, expansion additives, hardening accelerators (although, not normally required) and hardening retarders which may be particularly useful when high temperature environments are encountered. Portland cements having the small particle sizes required in this invention may require retardation of set time at elevated temperatures. Accordingly, conventional lignosulfonates are considered to be useful to achieve sufficient retardation. Still other additives may be utilized to still further decrease the slurry density of the cement composition of this invention. Such lightweight additives include nitrogen, perlite, fly ash, silica fume, microspheres and the like. It is believed that a combination of fine particle size cement, water and additives can produce a competent slurry having a density of as low as about 9 pounds per gallon which will achieve compressive strength sufficient for oil field operations.

When well cementing environments exhibit high temperatures, e.g. about 230 °F or more, it may be necessary to combine with the slurry a material which will help prevent the loss of compressive strength of set cement over time - a condition referred to as compressive strength retrogression. In one specific embodiment, a cement placed in a cased hole adjacent a geothermal formation or a formation into which steam will be introduced can be subjected to temperatures of up to about 600 °F. Such extremely high temperatures can produce a loss in compressive strength of set cement; however, by using the fine particle size, preferably Portland cement of this invention in combination with Silica Flour, a crystalline form of silicon dioxide (SiO₂), compressive strength retrogression can be prevented or at least reduced in magnitude. This material is added to the slurry in an amount effective to react with the hydraulic cement to help prevent the development of compressive strength retrogression. It is believed that such an effective amount is in the range of from about 0.15 to about 1.0 and preferably about 0.35 pounds silica flour per pound of hydraulic cement.

Still another advantage of this invention in addition to light weight slurries, low viscosity, good compressive strength, and small particle size are the thixotropic properties displayed by the slurry. Accordingly, with a slurry preferably consisting solely of small particle size Portland cement used in primary cementing operations the thixotropic properties help prevent unwanted fluid migration, especially unwanted gas migration, during the time when the cement is in an unset plastic condition.

The tables which follow provide information and data concerning the chemical, physical and performance properties of four hydraulic cements. Three of the cements are Portland cements and the fourth is a slag cement. One of the cements, identified as API Class A, due to particle size only, is not within the scope of this invention. The remaining three cements are within the scope of this invention.

Tables I and II provide physical data including specific surface, specific gravity, blending, and particle size analysis.

Tables III and IV provide performance data including compressive strength developed by stated slurries and penetration by stated slurries.

Tables V, VI, VII and VIII provide chemical content as determined by various different analysis techniques.

Table IX provides a chemical analysis of Portland type III cement as disclosed in U.S. Patent 4,160,674 to Sawyer.

TABLE I

Comparison of Cements				
Hydraulic Cement Name	Type	Specific Surface Blaine, cm^2/g	Specific Gravity g/cc	Slag Content Weight %
Ultra Fine	Portland	13080	3.03	0
API Class A	Portland	3900	3.15	0
White	Portland	6460	3.03	0
MC-500	SLAG/Portland	8960	2.95	80 to 90

TABLE II
Comparison of Cements

Hydraulic Cement Name	Type	Maximum Microns	Particle Size Analysis* Percent Passing Opening Microns														
			45.0	40.4	30.4	20.4	17.8	17.0	15.0	9.6	9.2	7.8	6.4	5.2	4.5	3.5	3.0
Ultra Fine Portland	11		-	-	-	-	-	-	100	-	-	-	90	79.1	-	50	33.4
API																	
Class A Portland	90		95	90	-	50	-	-	42.7	-	-	20	-	12.0	-	-	2.8
White Portland	27		-	100	90	-	-	-	74	-	50	-	-	27	-	20	8.9
MC-500 SLAG/ Portland	17		-	-	-	-	100	-	90	-	-	-	-	56.5	50	-	22.3
																20	5.4

* Malvern 3600 Bc Particle Size Analyzer

TABLE III

Comparison of Properties of Water Slurries of Hydraulic Cements

Hydraulic Cement Name	Type	1500 psi Compressive Strength After 24 hours Set @ 80°F		250 ^a psi Compressive Strength After 24 hours Set @ 80°F	
		lb Cement lb Water		lb Cement lb Water	
		Density, lb/gal		Density, lb/gal	
Ultra Fine	Portland	1.00	1.00	1.00	1.41
API					11.5
Class A	Portland	1.00 ¹	0.576	1.00 ⁴	0.99
					12.3
White	Portland	1.00 ²	0.80	1.00	1.17
					12.0
MC-500	SLAG/Portland	³	³	1.00	1.00
					12.5

Notes:

- ¹ 0.02 lb Bentonite, 0.01 lb Calcium Chloride
- ² 0.01 lb CFR-3 Dispersant
- ³ For practical commercial usages a slurry of sufficiently high density cannot be made to produce the indicated compressive strength
- ⁴ 0.39 lb Amorphous Silica, 0.39 lb Pozmix, 0.01 lb Calcium Chloride
- ⁵ The Texas Railroad Commission requirement for primary cementing of surface casing

TABLE IV

Comparison of Properties of Water Slurries of Hydraulic Cements

Hydraulic Cement Name	Type	Penetration of Slurry Through* A 2 Inch Long, 0.003 Inch Wide Slot Under Pressure of 90 psi		Cement lb	Water lb	Slurry ² Density lb/gal	Strength, 24 Hours psi
		Volume, cc	Time, Sec				
Ultra Fine Portland		10	2	7.1	1.00	1.41	250
API Class A		0.7	2	0.5	1.00	0.461	1900
White		3	2	2.2	1.00 ¹	1.00	750
MC-500		8.6	2	6.1	1.00	1.00	250

Notes:

¹ 0.01 lb CFR-3 Dispersant² The selected densities are considered to be commercial standards based on water required to avoid excessive settling of solids - i.e. water separation. Water requirements are a function of cement fineness.³ Density of 12.5 is not commercially practical due to excessive settling

*Note:

Penetration tests were conducted by pouring 140 ccs of slurry into a cell containing a hardened steel plate on the bottom. A slot of 0.003 inches in width was placed across the entire 2 inch diameter of the plate. A pressure of 90 psi was applied to force the cement slurry through the slot. The percentages are by volume of the total slurry placed in the cell. For example, since 140 ccs of the Capitol Ultra Fine was placed in the cell, 7.1%, or 10 ccs, passed through the slot before bridging off.

TABLE V

X-ray Fluorescence Analysis of Hydraulic Cement Material				
Oxide Components	Hydraulic Cement Name Percent			
	MC-500	Ultra Fine	API Class A	White
Na ₂ O	0.30	0.17	0.37	0.37
MgO	3.40	1.10	1.30	2.40
Al ₂ O ₃	11.29	4.26	4.32	4.01
SiO ₂	29.54	17.80	20.86	21.08
SO ₃	2.15	7.85	2.98	3.40
K ₂ O	0.41	0.95	0.93	0.27
CaO	50.79	62.12	65.29	65.64
TiO ₂	0.49	0.18	0.23	0.12
Cr ₂ O ₃	0.0	0.0	0.0	0.0
MnO	0.38	0.03	0.03	0.02
Fe ₂ O ₃	1.16	2.30	2.35	0.29
ZnO	0.01	0.01	0.02	0.01
SrO	0.08	0.11	0.07	0.04
Loss On Ignition	0.0	3.12	1.25	2.35

TABLE VI

Compound	Cement Compound Concentration, Percent By Bogue Calculation From Oxide Components in Table V			
	MC-500	Ultra Fine	API Class A	White
Free Lime	0.4	0.7	0.58	3.67
C ₃ S	*	62.56	64.89	55.58
C ₂ S	*	5.47	11.6	19.96
C ₃ A	*	7.63	7.57	10.39
C ₄ AF	*	7.22	7.23	0.89
CaSO ₄ (CS)	*	13.78	5.12	5.92
*Cannot Calculate due to excess of Al and Si				

TABLE VII

Quantitative X-Ray Diffraction Analysis
Hydraulic Cement Materials

Extract Component	Crystalline Compound	Hydraulic Cement Name			
		NC-500 %	Ultra Fine %	API Class A %	White %
Silicates	C ₃ S	*	74.0	79.9	81.7
	C ₂ S	*	41.5	52.0	55.6
Sulfates		*	32.5	27.9	26.1
	CaSO ₄ ·2H ₂ O	*			
	CaSO ₄ ·1/2H ₂ O	*	10.6	4.6	4.8
	Syngenite	*	4.7	0.4	1.9
Alumino Ferrites		*	2.5	1.6	3.4
		*	3.4	2.6	-
		*			
		*	15.4	15.5	13.5
	C ₃ A ¹	*	7.7	4.6	8.5
	C ₃ A ²	*	1.1	2.8	4.0
	C ₄ AF	*	6.4	7.8	-
	Periclase	*	0.1	0.2	0.8
	Dolomite	*	0.1	0.1	-
	Quartz	*	-	-	0.2

*Compounds are primarily non-Crystalline and therefore cannot be examined quantitatively

¹ Cubic Crystalline form

² Orthorhombic Crystalline form

TABLE VIII

Miscellaneous Information
Hydraulic Cement Name

Measurement	NC-500 %	Ultra Fine %	API Class A %	White %
Insoluble Residue	0.24	0.09	0.16	0.41
Total Alkali	0.57	0.80	0.98	0.55
Total H ₂ O Sol. Alkali	0.56	0.05	0.43	0.17
Differential Thermal Analysis				
Gypsum	0.0	5.44	0.30	0.85
Hemihydrate	1.04	0.44	0.17	0.88

Referring now to Tables I, II, III, IV, V, VI, VII, and VIII set out above, there is presented, in convenient
 55 tabular form, a comparison of various properties of four different cementitious materials each of which
 exhibit hydraulic activity. "Hydraulic activity" and "reactivity" as used herein mean the chemical nature of a
 material to set and harden, upon being mixed with water, without contact with the atmosphere (e.g. the
 ability to harden under water) due to the interaction of the constituents of the material rather than by

evaporation of the water. The term "hydraulic cement" as used herein means all inorganic cementitious materials of known type which comprise compounds of calcium, aluminum, silicon, oxygen and/or sulfur which exhibit "hydraulic activity", that is, which set solid and harden in the presence of water. Cements of this type include common Portland cements, fast setting or extra fast setting, sulfate resistant cements, modified cements, alumina cements, high alumina cements, calcium aluminate cements, and cements which contain secondary components such as fly ash, pozzalona and the like. See for example Roca, et al., U.S. 4,681,634. There are in existence inorganic cementitious materials other than those exemplified in Tables I - VIII which exhibit hydraulic activity, but this invention is preferably limited to the types included in Tables I - VIII.

Accordingly, Portland cement, one of the materials listed in the Tables is made by sintering (thermally treating) a ground mixture of raw materials one of which is usually composed mainly of calcium carbonate (as limestone) and another of which is usually composed mainly of aluminum silicates (as clay or shale) to obtain a mixture of lime, aluminum oxide, silicon dioxide and ferric oxide. During the sintering process chemical reactions occur which produce nodules, called clinkers, which are primarily composed of mixed calcium silicates (C_2S and C_3S), calcium aluminates (C_3A) and calcium aluminoferrites (C_4AF) all of which compounds contribute to the hydraulic activity of Portland cement. See for example Braunauer, U.S. 3,689,294; Buchet, et al., U.S. 4,054,460; and Gartner, U.S. 4,619,702. An example of a chemical analysis of Portland cement clinker is provided by Skvåra, U.S. 4,551,176 as follows:

<u>Component</u>	<u>Weight Percent</u>		
SiO_2	20	-	21.9
CaO	62.2	-	67.3
Al_2O_3	4.7	-	6.3
Fe_2O_3	2.4	-	4.5
MgO	1.3	-	3.3
SO_3	0.16	-	1.05
$Na_2O + K_2O$	0.81	-	0.95

After sintering, the clinkers are ground together with additives, including for example a quantity of calcium sulfate dihydrate (gypsum) to control set time, to a specific surface area, sometimes called Blaine Fineness, of as high as 10,000 $cm^2/gram$ or more, but ordinarily the grinding is sufficient to produce a specific surface area in the range of from about 2500 to 5000 $cm^2/gram$ with 3000 to 4500 $cm^2/gram$ being the usual Blaine Fineness range for Portland cement. See for example Gartner, U.S. 4,619,702; Miyoshi, et al., U.S. 4,443,260; Buchet, et al., U.S. 4,054,460; and Braunauer, U.S. 3,689,294.

Portland cements are classified by the American Society of Testing Materials (ASTM) into five major types identified by Roman Numerals I, II, III, IV and V and by the American Petroleum Institute into at least 9 categories identified by the letters A, B, C, D, E, F, G, H and J. The classifications are based on chemical composition and physical properties.

Sawyer in U.S. 4,160,674 specifically discloses a Type III Portland cement exhibiting high early compressive strength wherein: substantially all particles in the cement are of a size of about 20 microns and smaller; the Blaine Fineness is about 8990 $cm^2/gram$; and the specific gravity is 3.00. Sawyer provides an analysis of the Type III material, which is referred to as the "fine product". The analysis is set out in Table IX below.

Table IX

<u>Chemical Analysis-Fine Product</u>			<u>Compound Composition</u>	
5	SiO ₂	19.61	C ₃ S	46.58
	Al ₂ O ₃	4.93	C ₂ S	21.10
	Fe ₂ O ₃	2.50	C ₃ A	8.83
10	CaO	61.26	C ₄ AF	7.61
	MgO	1.42	CaSO ₄	10.18
15	SO ₃	5.99		
	Loss	3.12		
	Total	98.83		
20		Lime Factor	2.45	
		Silica Ratio	2.64	
25		A/F	1.97	
		Insol Residue	0.53	
		Free CaO	1.26	
30		Na ₂ O	0.11	
		K ₂ O	1.06	
35		Total alk.	0.81	

40 Galer, et al., in U.S. 4,350,533 provides abbreviations for chemical formulas of cement compounds in accordance with general practice in the cement industry as follows:

C represents calcium oxide (CaO)
 A represents aluminum oxide (Al₂O₃)
 F represents ferric oxide (Fe₂O₃)
 M represents magnesium oxide (MgO)
 45 S represents silicon dioxide (SiO₂)
 K represents potassium oxide (K₂O)
 N represents sodium oxide (Na₂O)
 H represents water (H₂O)
 S represents sulfur trioxide (SO₃)
 50 C represents carbon dioxide (CO₂)

Accordingly, based upon the above abbreviations the chemical composition of the Type III Portland cement disclosed by Sawyer (Table IX above) is:

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C_3S	: $3CaO \cdot SiO_2$	46.58
C_2S	: $2CaO \cdot SiO_2$	21.10
C_3A	: $3CaO \cdot Al_2O_3$	8.83
C_4AF	: $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	7.61
CS	: $CaSO_4$	10.18

Tables I - VIII also include a hydraulic cement material identified as "Slag/Portland" which is a combination of Portland cement and slag.

"Slag", as used herein, means a granulated, blast-furnace, by-product formed in the production of cast iron and is broadly comprised of the oxidized impurities found in iron ore.

During the operation of a blast furnace to remove iron from iron ore a molten waste product is formed. By preventing this molten product from crystallizing, and thereby losing its energy of crystallization, a super-cooled liquid or non-crystalline glassy material can be formed thus retaining the energy of crystallization. This non-crystalline, glassy material, which has also been described as a vitreous substance free from crystalline substances as determined by X-ray diffraction analysis, is said to be capable of exhibiting hydraulic activity upon being reduced in size by grinding from a particle size of 1 to 5 millimeters to a fine particle size in the range of from about 1 to about 100 microns. Many commentators, including Clarke in U.S. 4,761,183 and Forss in U.S. 4,306,912, state that the glass content of the material, in order to exhibit latent hydraulic activity, must be high and preferably above about 95 percent.

Crystallization of the molten blast-furnace waste product can be prevented and the super cooled liquid or glass can be formed by rapidly chilling the molten waste. This rapid chilling can be effected by spraying the molten waste with streams of water which operation causes rapid solidification and formation of a water slurry of small, glassy, sand-like particles. The slurry is then thermally dried to remove substantially all moisture to thereby produce a dry blend of coarse particles. This dry blend of particles, having a particle size in the range of 1 to 5 millimeters, is then ground to reduce particle size to values in the range of from 1 to about 100 microns and preferably less than about 325 mesh (45 microns) to produce the granulated, blast-furnace by-product herein defined as "Slag". See, for example, Miyoshi, et al., U.S. 4,443,260; Allemand, et al., U.S. 3,809,665;

Buchet, et al., U.S. 4,054,460; Gee, et al., U.S. 4,242,142; Clarke, U.S. 4,761,183; and Forss, U.S. 4,306,912.

Clarke '183 and Miyoshi, et al., in U.S. 4,306,910 disclose the following analysis, said by them to be representative of the usual ranges of chemical content of slag.

		<u>Weight Per Cent</u>	
	<u>Component</u>	<u>Clarke</u>	<u>Miyoshi</u>
5	SiO ₂	30-40	30 - 35
	Al ₂ O ₃	8-18	13 - 18
	Fe ₂ O ₃	-	0.5 - 1.0
10	CaO	35-50	38 - 45
	MgO	0-15	3 - 6
15	SO ₃	-	-
	FeO	0-1	-
	S	0-2	0.5 - 1.0
20	Mn ₂ O ₃	0-2	-
	MnO	-	0.5 - 1.5
25	TiO ₂	0	0.5 - 1.0

Clarke further states that the density of slag is considered to be 2.92 grams per cubic centimeter. Another analysis of slag is provided by Yamaguchi, et al., in U.S. 3,904,568 as follows:

	<u>Component</u>	<u>Weight Per Cent</u>
30	SiO ₂	34.9
	Al ₂ O ₃ + Fe ₂ O ₃	16.8
35	CaO	41.1
	MgO	5.5

Miyoshi, et al., '910 state that the hydraulic activity of slag is low if the particle size of the slag is in the range of 1 to 5 millimeters and accordingly, suggest that the particle size of slag should be reduced by grinding to a value of at least about 5 microns or less; and still further state that the slag, by itself, even after grinding has no or very low hydraulic activity and thus requires activation or stimulation such as by the addition thereto of slaked lime (CaO·H₂O). Other additives to stimulate or activate the hydraulic activity of Slag include sodium hydroxide, sodium sulfate sodium carbonate, sodium silicate, potassium sulfate and Portland cement. See for example Clarke, U.S. 4,761,183 and Clarke, U.S. 4,897,119.

According to Forss in U.S. 4,306,912 grinding slag to a high specific surface, e.g. in the range of from about 4000 to about 8000 cm²/gram, can increase the hydraulic activity and hardening rate of the material. Forss also states that it is known that grinding cement clinker beyond a certain limit is not beneficial because additional fineness hardly improves the properties of hardening and strength. On the other hand Birchall, et al., in U.S. 4,353,747 state that the strength of Portland cement can be improved by reducing the weight average mean particle size of Portland cement to a value of less than 20 microns.

The various methods for conducting cementing operations normally associated with wells in subterranean hydrocarbon producing formations are generally known. These basic techniques with changes, as required, can be employed to place the fine particle size cement of this invention in position to solve the various problems addressed herein.

The preferred method of cementing primary oil field casings using ultra fine cement slurries include conductor pipe, surface casing, intermediate casing, production casing, drilling linet, production liner, scab liner, and tieback casing, is as follows:

1. Pump the slurry or any preceding or following fluid down the casing (tubing or drill pipe) and back up the annular space between the casing and the drilled hole.
2. (optional) Precede all fluids with a "bottom" wiper plug to clean drilling fluid from the casing.
3. (optional) Pump a preflush chemical wash or "spacer" to serve as a drilling fluid removal agent and as a compatible spacer between the drilling fluid and the cement slurry.
4. Pump the cement slurry.
5. (optional) Follow the cement slurry with a conventional cement slurry.
6. Follow the cement slurry with a "top" wiper plug.
7. Pump a commonly used displacement fluid (water, drilling fluid, e.g.) to force the cement slurry down the casing and up into the annulus. Pump enough fluid to displace the required amount of casing volume. The "top" plug should land on a baffle or "float collar", closing off the flow of fluid to the annulus.
8. Pressure up to ensure that the top plug has landed.
9. Release pressure on casing to test if the "float" is holding to keep the cement in the annulus.
10. Terminate any operation in the wellbore for a time sufficient to permit the cement to set (WOC).

20 Claims

1. A method of fixing a cylinder in the interior of a bore, wherein said cylinder is situated in said interior of said bore so as to define a space between the exterior of said cylinder and the wall of said bore, said method comprising the steps of introducing into said space a volume of a slurry of a hydraulic cement; maintaining said volume of said slurry in said space for a time sufficient to enable said slurry to form a sheath of rigid cement in said space to thereby fix said cylinder in said interior of said bore; characterized in that the said slurry comprises a mixture of water and hydraulic cement in the weight ratio of 0.5:1 to 5.0:1, the particle size of the cement being no greater than 17 microns, and the Blaine Fineness of the cement being no less than 7000 cm²/g, and wherein 90% of the particles have a diameter not greater than 10 microns, 50% of said particles have a diameter not greater than 6 microns and 20% of said particles have a diameter not greater than 3 microns.
2. A method according to claim 1, wherein said hydraulic cement is a blend of slag and Portland cement, said bore is a well bore penetrating a subterranean earth formation, said cylinder is a well casing suspended in said well bore and said space is the annular space between said cylinder and said well bore.
3. A method according to claim 1 or 2, wherein the said weight ratio of water to cement is from 1.0:1 to 1.75:1.
4. A method according to claim 1,2 or 3, wherein the bore is a well bore penetrating a subterranean earth formation having a temperature in excess of 230°F (110°C) and said slurry additionally contains an effective amount of silica flour to help prevent the development of compressive strength retrogression of the set cement.
5. A method according to claim 4, wherein the quantity of said silica flour is from 0.15 to 1.0 parts by weight of silica flour per part by weight of cement.
6. A method according to claim 5, wherein the temperature of said subterranean earth formation is up to 600°F (316°C).
7. A method according to any preceding claim, wherein said cement is Portland cement.
8. A method according to claim 7, wherein the maximum particle size of the Portland cement is 11 microns, the Blaine Fineness is 10,000 cm²/g, 90% of said particles have a diameter not greater than 7 microns, 50% of said particles have a diameter not greater than 4 microns and 20% of said particles have a diameter not greater than 2 microns.



The preferred method of cementing primary oil field casings using ultra fine cement slurries include conductor pipe, surface casing, intermediate casing, production casing, drilling linet, production liner, scab liner, and tieback casing, is as follows:

1. Pump the slurry or any preceding or following fluid down the casing (tubing or drill pipe) and back up the annular space between the casing and the drilled hole.
2. (optional) Precede all fluids with a "bottom" wiper plug to clean drilling fluid from the casing.
3. (optional) Pump a preflush chemical wash or "spacer" to serve as a drilling fluid removal agent and as a compatible spacer between the drilling fluid and the cement slurry.
4. Pump the cement slurry.
5. (optional) Follow the cement slurry with a conventional cement slurry.
6. Follow the cement slurry with a "top" wiper plug.
7. Pump a commonly used displacement fluid (water, drilling fluid, e.g.) to force the cement slurry down the casing and up into the annulus. Pump enough fluid to displace the required amount of casing volume. The "top" plug should land on a baffle or "float collar", closing off the flow of fluid to the annulus.
8. Pressure up to ensure that the top plug has landed.
9. Release pressure on casing to test if the "float" is holding to keep the cement in the annulus.
10. Terminate any operation in the wellbore for a time sufficient to permit the cement to set (WOC).

Claims

1. A method of fixing a cylinder in the interior of a bore, wherein said cylinder is situated in said interior of said bore so as to define a space between the exterior of said cylinder and the wall of said bore, said method comprising the steps of introducing into said space a volume of a slurry of a hydraulic cement; maintaining said volume of said slurry in said space for a time sufficient to enable said slurry to form a sheath of rigid cement in said space to thereby fix said cylinder in said interior of said bore; characterized in that the said slurry comprises a mixture of water and hydraulic cement in the weight ratio of 0.5:1 to 5.0:1, the particle size of the cement being no greater than 17 microns, and the Blaine Fineness of the cement being no less than 7000 cm²/g, and wherein 90% of the particles have a diameter not greater than 10 microns, 50% of said particles have a diameter not greater than 6 microns and 20% of said particles have a diameter not greater than 3 microns.
2. A method according to claim 1, wherein said hydraulic cement is a blend of slag and Portland cement, said bore is a well bore penetrating a subterranean earth formation, said cylinder is a well casing suspended in said well bore and said space is the annular space between said cylinder and said well bore.
3. A method according to claim 1 or 2, wherein the said weight ratio of water to cement is from 1.0:1 to 1.75:1.
4. A method according to claim 1,2 or 3, wherein the bore is a well bore penetrating a subterranean earth formation having a temperature in excess of 230 °F (110 °C) and said slurry additionally contains an effective amount of silica flour to help prevent the development of compressive strength retrogression of the set cement.
5. A method according to claim 4, wherein the quantity of said silica flour is from 0.15 to 1.0 parts by weight of silica flour per part by weight of cement.
6. A method according to claim 5, wherein the temperature of said subterranean earth formation is up to 600 °F (316 °C).
7. A method according to any preceding claim, wherein said cement is Portland cement.
8. A method according to claim 7, wherein the maximum particle size of the Portland cement is 11 microns, the Blaine Fineness is 10,000 cm²/g, 90% of said particles have a diameter not greater than 7 microns, 50% of said particles have a diameter not greater than 4 microns and 20% of said particles have a diameter not greater than 2 microns.



9. A method according to claim 8, wherein the C_3A crystalline content of the Portland cement is at least 3.0% by weight of said cement, and the sulfate content of the Portland cement is at least 1.0% by weight of said cement.

5 Patentansprüche

1. Eine Vorgangsweise zum Befestigen eines Zylinders im Innenraum einer Bohrung, wobei besagter Zylinder so im Inneren besagter Bohrung ausgeführt ist, daß sich zwischen besagter Außenseite besagten Zylinders und der Bohrlochwand ein Hohlraum bildet. Besagte Vorgangsweise besteht aus den Schritten der Einführung einer Menge Schlamm aus hydraulischem Zement in besagten Hohlraum; Beibehalten besagten Volumens besagten Schlamms im besagten Hohlraum für einen Zeitraum, der ausreicht, um das Bilden eines Mantels aus starrem Zement im besagten Hohlraum durch besagten Schlamm zu ermöglichen, um so besagten Zylinder im besagten Innenraum besagter Bohrung abzusichern; gekennzeichnet dadurch, daß besagter Schlamm aus einer Mischung von Wasser und hydraulischem Zement im Gewichtsverhältnis 0,5:1 bis 5,0:1 besteht, wobei die Partikelgröße des Zements nicht größer ist als 17 Mikron und die Blainesche Feinheit des Zements nicht unter 7.000 cm^2/g liegt, während 90 % der Partikel einen Durchmesser nicht größer als 10 Mikron, 50 % besagter Partikel einen Durchmesser nicht größer als 6 Mikrons und 20 % besagter Partikel einen Durchmesser nicht größer als 3 Mikrons aufweisen.
2. Eine Vorgangsweise nach Anspruch 1, wobei besagter hydraulischer Zement eine Mischung aus Schlacke und Portlandzement, besagte Bohrung ein Bohrloch, das eine unterirdische Formation durchdringt, besagter Zylinder eine im besagten Bohrloch suspendierte Bohrlochverrohrung und besagter Hohlraum der Ringraum zwischen besagtem Zylinder und besagtem Bohrloch ist.
3. Eine Vorgangsweise nach Anspruch 1 oder 2, wobei besagtes Gewichtsverhältnis von Wasser und Zement von 1,0:1 bis 1,75:1 ist.
4. Eine Vorgangsweise nach Anspruch 1, 2 oder 3, wobei die Bohrung ein Bohrloch ist, das eine unterirdische Erdformation mit Temperatur im Bereich über 110° C ist und besagter Schlamm zusätzlich eine wirksame Menge von Silikatismehl enthält, mit der die Verhinderung der Entwicklung von Druckfestigkeitsretrogression des gehärteten Zements gefördert wird.
5. Eine Vorgangsweise nach Anspruch 4, wobei die Menge besagten Silikatismehls im Bereich 0,15 bis 1,0 Teile nach Gewicht von Silikatismehl pro Gewichtsteil Zement liegt.
6. Eine Vorgangsweise nach Anspruch 5, wobei die Temperatur besagter unterirdischer Erdformation bis zu 316° C ist.
7. Eine Vorgangsweise nach einem der o.g. Ansprüche, wobei besagter Zement Portlandzement ist.
8. Eine Vorgangsweise nach Anspruch 7, wobei die maximale Partikelgröße des Portlandzements 11 Mikron und die Blainesche Feinheit 10.000 cm^2/g ist, während 90 % besagter Partikel einen Durchmesser nicht größer als 7 Mikrons, 50 % besagter Partikel einen Durchmesser nicht größer als 4 Mikrons und 20 % besagter Partikel einen Durchmesser nicht größer als 2 Mikrons haben.
9. Eine Vorgangsweise nach Anspruch 8, wobei der kristallinische C_3A -Gehalt des Portlandzements mindestens 3,0 % nach Gewicht besagten Zements und der Sulfatgehalt besagten Portlandzements mindestens 1,0 % nach Gewicht besagten Zements beträgt.

Revendications

1. Un procédé de fixation d'un cylindre à l'intérieur d'un forage, procédé dans lequel ledit cylindre est situé dans ledit intérieur du dit forage de manière à définir un espace entre l'extérieur du dit cylindre et la paroi du dit forage, ladite méthode comportant les étapes d'introduction dans ledit espace d'un volume d'un coulis d'un ciment hydraulique; le maintien du dit volume du dit coulis dans ledit espace pendant une durée suffisante pour permettre au dit coulis de former un cuvelage de ciment rigide à l'intérieur du dit espace, fixant ainsi ledit cylindre dans ledit intérieur du dit forage. Le procédé se



caractérise en ce que ledit coulis comporte un mélange d'eau et de ciment hydraulique dans une proportion de poids de 0,5:1 à 5,0:1, la granulométrie du ciment n'excédant pas 17 microns et la finesse Blaine du ciment n'étant pas inférieure à 7000 cm²/g, et dans lequel 90% des particules ont un diamètre n'excédant pas 10 microns, 50% des dites particules ayant un diamètre n'excédant pas 6 microns et 20% des particules ayant un diamètre n'excédant pas 3 microns.

- 5 2. Un procédé selon la revendication 1, dans lequel ledit ciment hydraulique est un mélange de laitier et de ciment Portland, ledit forage est un forage de puits pénétrant à travers une formation souterraine, ledit cylindre est un tubage de puits suspendu dans ledit forage et ledit espace est l'espace annulaire
10 entre ledit cylindre et ledit forage.
3. Un procédé selon la revendication 1 ou 2, dans lequel ladite proportion de poids entre l'eau et le ciment se situe entre 1,0:1 et 1,75:1.
- 15 4. Un procédé selon la revendication 1, 2 ou 3, dans lequel le forage est un forage de puits pénétrant une formation souterraine dont la température excède 230 °F (110 °C) et ledit coulis contient additionnellement une quantité efficace de poudre de silice pour aider à empêcher la survenue d'une rétrogression de la résistance à la compression du ciment après la prise.
- 20 5. Un procédé selon la revendication 4, dans lequel la quantité de ladite poudre de silice va de 0,15 à 1,0 partie par poids de poudre de silice par partie par poids de ciment.
6. Un procédé selon la revendication 5, dans lequel la température de ladite formation souterraine atteint 600 °F (316 °C).
- 25 7. Un procédé selon l'une quelconque des revendications précédentes, dans lequel ledit ciment est du ciment Portland.
- 30 8. Un procédé selon la revendication 7, dans lequel la granulométrie maximum du ciment Portland est de 11 microns, la finesse Blaine de 10.000 cm²/g, 90% des dites particules ayant un diamètre n'excédant pas 7 microns, 50% des dites particules ayant un diamètre n'excédant pas 4 microns et 20% des dites particules ayant un diamètre n'excédant pas 2 microns.
- 35 9. Un procédé selon la revendication 8, dans lequel la teneur en C₃A cristallin du ciment Portland est de 3,0% au minimum par poids du dit ciment, et la teneur en sulfate du ciment Portland est au minimum 1,0% par poids du dit ciment.