

Description

This invention relates to cementing compositions and their use in oil wells and the like.

For oil field cementing operations to be successful, additives which reduce fluid loss are required to be added to the cement. Such additives will be used in well cementing operations where the bottom hole circulating temperatures (BHCT) may range from 80° to 170° F (27° to 77° C), substantial salt concentrations may be present, and slurry retardation and viscosity are critical aspects because they affect pumpability and compressive strength.

Certain polymer compositions have long been recognised as useful in reducing fluid loss from a slurry of cement and water to the surrounding environment, i.e. the formation. These compositions are commonly referred to as "fluid loss additives".

An example of a fluid loss additive for use in an acidizing or fracturing composition is found in U.S. patent specification no. 4,107,057. In this specification a copolymer of a sulfonic-acid modified acrylamide and a polyvinyl cross-linking agent is employed.

In the oil well cementing art, a variety of polymers have been described as useful fluid loss additives for hydraulic oil well cements. For example, U.S. patent specification no. 4,015,991 describes such a fluid loss additive for a hydraulic cement slurry consisting of hydrolysed copolymers of acrylamide (AA) and 2-acrylamido-2-methyl propane sulfonic acid (AMPS). However, these AA/AMPS copolymers are useful only in operations where the bottom hole circulating temperature (BHCT) ranges from 90° to 125° F (32° to 52° C), whereas BHCT ranges encountered in such operations are often outside such a range. Still further, these copolymers have a salt tolerance of only up to about 10%.

The temperature limitations of the AA/AMPS copolymers, i.e. loss of usefulness above about 125° F (52° C) BHCT, are believed to be the result of hydrolysis of the amide groups. The carboxylate groups formed by such hydrolysis convert the copolymers to materials which function to retard the setting of the cement and to reduce the compressive strength of the set cement. Further, in the lower portion of the above-mentioned temperature range (between 90° and 100° F (32° and 38° C)) the AA/AMPS is less effective as a fluid loss additive, requiring inclusion of larger amounts of such additive than at higher temperatures. The inclusion of a sufficiently large amount of additive to create an acceptable fluid loss composition often creates viscosity and pumpability problems, since the addition of such copolymer directly affects the resultant slurry rheology. Copolymers of acrylamide and AMPS exhibit high viscosity and poor mixability, resulting in cement slurries having poor pumpability characteristics during cementing operations. Mixability is a subjective term used to describe how well the components in the cement composition wet and mix with each other, as well as the energy required to create a generally homogeneous slurry.

Hence, the industry desires a fluid loss additive that has as little effect on compressive strength, set time, viscosity and thickening time as possible; is salt tolerable, i.e. does not exhibit substantial loss of effectiveness in the presence of salt; and is chemically stable during cementing operations. Further, such desired fluid loss additive should be compatible with as many other additives and environmental conditions as possible, should be soluble in cement slurries at normal ambient temperature encountered in oil well cementing operations, as well as to continue to provide fluid loss characteristics over broad temperature and cement pH range.

U.S. specification no. 4,404,111 discloses the use of copolymers of N,N-dimethylacrylamide and 2-acrylamido-2-methyl propane sulfonic acid as viscosity control agents in aqueous compositions to facilitate petroleum recovery from subterranean bearing formations. The method of preparing said copolymers uses conventional free radical initiators such as ammonium persulfate and results in copolymers having average molecular weights of greater than about one million. Further, the amount of NNDMA monomer employed in preparing the AMPS/NNDMA copolymer is disclosed as between 70 and about 99.5 weight percent.

We have now devised certain cementing compositions for use in oil, gas and water well cementing operations. More particularly, these compositions are comprised of water, hydraulic cement and certain copolymer salts, the copolymers being of N,N-dimethylacrylamide (NNDMA) and 2-acrylamido-2-methyl propane sulfonic acid or salt (AMPS). Such copolymer salts are fluid loss additives having a NNDMA/AMPS monomer ratio of between 4:1 and 1:4 and an average molecular weight of from about 75,000 to 300,000. These copolymer salts are relatively stable to hydrolysis over a wide range of temperature and pH. They may be admixed in solid form with any dry hydraulic oil field cement, or may be added at the time the cement slurry is being prepared, either to the mixing water or to the slurry. Additionally, methods of cementing a conduit in a borehole penetrating an earthen formation by introducing such a cementing composition into the space between such conduit and formation are described. These copolymer salts are also used in a cementing method which is the subject-matter of our application 86307232.8 published as EP-A-0 217 608.

The copolymer salts can be made by, for example, neutralising the copolymer acid or by making the copolymer from an acid salt monomer. The preferred cations are calcium, magnesium and ammonium.

The Brookfield viscosity reading of a 1000 ppm aqueous solution of the copolymer salts used in the present invention, at 5 r.p.m. using a U.L. Adapter Spindle is in the range between about 30 and about 250 centipoise (.03 and .25 Pa s). Preferably, the Brookfield viscosity reading is between about 130 and about 200 centipoise (.13 and .20 Pa s). Further, where the compositions contain common salt (sodium chloride) in an amount up to about 18% by weight of water, then the preferred mole ratio of NNDMA to AMPS is about 1:1.5. Numerous copolymer salts can be made, but where cementing compositions contain common salt (sodium chloride) in an amount up to about 18% by weight of water are utilised, the preferred copolymer salt is one made by neutralisation of the acid form of the AMPS monomer or NNDMA/AMPS copolymer with an alkaline agent such as a source of calcium, magnesium or ammonium ions. Such alkaline agents can comprise, for example, calcium hydroxide, ammonia, magnesium hydroxide and the like.

The cementing compositions of the present invention are useful in oil, gas and water well cementing operations since such compositions have reduced fluid loss to the surrounding formation. Such compositions are used to cement a conduit penetrating a permeable earthen formation by introducing the composition into the space between the conduit and the formation, and allowing the composition to harden.

The copolymer salts used in the present invention may be manufactured in accordance with various well known free-radical techniques. However, in the present invention solution polymerisation techniques were employed to obtain polymer solutions of NNDMA and AMPS containing 10% by weight of solids. The mole ratio of the NNDMA to AMPS monomers can vary within the limits of 4 to 1 in either direction.

The salts of the copolymers may be produced in accordance with the various well known techniques. The salt may be formed, for example, by reaction of an alkaline agent with either the AMPS monomer before polymerisation or the NNDMA/AMPS copolymer. The salt may be formed with an alkaline agent which does not adversely react with the monomers of the copolymer or the other constituents present in the cementing composition.

Two NNDMA/AMPS copolymers were tested as fluid loss additives. These tests were performed at 100° F (38° C) using Class H cement and 46% water by weight of dry cement. The additive containing cement slurries were mixed in a Halliburton Consistometer and stirred for twenty minutes. The Halliburton Consistometer is a non-pressurised device that simulates a cementing pumping process via movement of the consistometer can about a paddle. Temperature can be varied but pressure is atmospheric. Fluid loss was measured at 1000 psi (6.9 MPa) through a 325 mesh (U.S. Standard) screen in cm³/30 min. The results of these fluid loss tests are provided in Table I.

The Table I test results indicate that the two copolymers are effective fluid loss additives under static 100° F (38° C) temperature conditions.

Table I
Fluid Loss Tests on Several Polymers
 Base Slurry - Class H Cement + 46% Water

Polymer Name	% Polymer By Weight Cement	Consistometer Reading 0 min	20 min	Fluid Loss
Copolymer of AMPS and NNDMA (1:1)	0.2	4	7	94
	0.4	9	9	28
Copolymer of AMPS and NNDMA (1:4)	0.6	9	9	34

To determine whether copolymers of AMPS/NNDMA are sensitive to temperature variations, tests were conducted in the same manner as above at temperatures of 80°, 100°, 125° and 172° F (27°, 38°, 52° and 78° C). Additionally, various mole ratios of AMPS/NNDMA were evaluated. The results, as provided in Table II, indicate that such copolymers of AMPS/NNDMA are effective fluid loss agents over a broad range of temperatures. Additionally, the data indicate that there is limited fluid loss variation with variation of the mole

ratio of AMPS/NNDMA when the amount of AMPS/NNDMA present remains constant at 0.6% by weight of dry cement.

Table II
Fluid Loss of Several AMPS - NNDMA
Copolymers of Varying Monomer Ratio

% of AMPS/NNDMA Copolymer by Wt. of Dry Cement	Mole Ratio AMPS/NNDMA	Halliburton Consistometer (Rheology at 0 Min./ Rheology after 20 Min.)					Fluid Loss			
		80°F (27°C)	100°F (38°C)	125°F (52°C)	172°F (78°C)		80°F (27°C)	100°F (38°C)	125°F (52°C)	172°F (78°C)
0.60	1:1.5	19/16	13/12	15/11	12/10		22	26	26	32
0.60	1.5:1	7/8	6/8	5/6	5/6		34	40	44	58
0.60	2:1	10/13	9/10	8/10	--		22	24	28	--
0.60	3:1	7/11	7/9	6/8	5/7		24	26	28	44
0.60	3.5:1	7/10	6/9	6/8	5/7		24	26	30	44

Base Slurry: Class H Cement + 46% H₂O by weight of dry cement.

Table III provides test results where the mole ratios of the AMPS NNDMA copolymers were varied between 1:4 and 3.5:1. Further, the slurries containing these copolymers contained in sea water or common

salt in an amount of 10%, 18% or sufficient to cause saturation. Although the data found in Table II indicate that variation in the mole ratio of AMPS/NNDMA present in fresh water slurries has little effect on fluid loss properties, results in salt water are much different. The data found in Table III indicate that the copolymers tested respond differently when common salt concentrations are varied. As the common salt concentration is increased, there is an increase in fluid loss. The copolymer additive was very effective when used in sea water slurries, with fluid loss variance measured between 26 and 46. In a 10% common salt by weight of water slurry, the fluid loss properties were excellent in the percent additive range of 0.8% or 1.0% by weight of dry cement, except for the 4:1 and 1:3.5 mole ratio of AMPS/NNDMA containing slurries. The slurries containing on 0.6% of additive by weight of dry cement were less effective. To maintain the degree of effectiveness, it is necessary to increase the amount of copolymer additive as the amount of common salt is increased. This is further illustrated in the 18% by weight of water and saturated common salt slurries. However, it should be noted that as the amount of copolymer additive is increased, the rheology of the slurry also increased. From an operations standpoint, slurries having a rheology measured above about 12-15 Bearden units of consistency on the Halliburton consistometer become less desirable and increasingly less desirable as that number increases.

Although the amount of copolymer present may be varied, a generally effective amount will be from about 0.1% to about 1.5% by weight of dry cement. Such an effective amount will depend on the amount of salt and water present, temperature, average molecular weight of the copolymer, rheological considerations and other additives present.

Table III

Fluid Loss and Viscosities of Various AMPS-NNDMA Copolymers
In Salt and Sea Water Slurries at 125°F (52°C) (Base slurry: Class II Cement + 46% Water by Wt. of Dry Cement)

Halliburton Consistometer										
Mole Ratio AMPS/NNDMA		% Additive by Wt. of Dry Cement	Rheology at 0 Min./Rheology After 20 Min.					Fluid Loss		
			Sea Water	10% Salt by Wt. of H ₂ O	18% Salt by Wt. of H ₂ O	Sat'd Salt	Sea Water	10% Salt	18% Salt	Sat'd Salt
1:4		0.6	12/12	11/15	10/11	10/9	36	143*	153*	464*
1:1		0.6	19/10	9/10	9/10	10/14	40	76	138*	421*
1.5:1		0.6	15/10	9/11	8/10	9/15	34	50	132	474*
2:1		0.6	9/8	7/8	9/12	10/12**	38	52	163*	563*
3.5:1		0.6	5/7	6/7	6/8	8/11	46	360*	468*	700*
1:1		0.8	—	14/14	12/15	12/17	—	28	40	312*
1.5:1		0.8	—	10/14	10/14	8/13	—	38	90	335*
2:1		0.8	14/15	10/11	9/11	10/14**	26	32	120	332*
1:1		1.0	—	20/20	15/19	13/17	—	22	24	168*
1.5:1		1.0	—	13/14	13/15	10/16	—	30	40	208*
2:1		1.0	—	11/12	10/11	10/19	—	28	48	179*
3.5:1		1.0	—	8/10	—	—	—	344*	—	—
1:4**		0.6	30/12	14/10	15/10	23/10	156	64	70	287

* Calculated

** Slurry tended to gel at the top of the Halliburton Consistometer paddle

*** This additive was a copolymer of AMPS and acrylamide having a mole ratio of 1:4 AMPS/acrylamide

When used in cement slurries containing appreciable amounts of common salt, the most preferred fluid loss additive copolymer of AMPS and NNDMA has a 1.5:1 AMPS/NNDMA mole ratio. Good fluid loss properties are exhibited when the mole ratio of NNDMA:AMPS is varied from about 4:1 to about 1:4. However, as the AMPS:NNDMA mole ratio is varied away from the about 1.5:1 most preferred range, the fluid loss characteristics in such salt-containing slurries are diminished. Such copolymers can be prepared

with a variety of molecular weights.

Table IV
Brookfield Viscosity Measurements of AMPS - NNDMA (1.5:1 mole ratio)
Copolymers of Varied Molecular Weights

Sample	Percent of Polymer in Solution	Brookfield Viscosity* of a 1000 ppm polymer solution at			Viscosity in Centipoise (Pa s) of a 1000 ppm polymer solution at		
		1 rpm	2.5 rpm	5 rpm	1 rpm	2.5 rpm	5 rpm
(1)	10	18	41	77.5	288 (.288)	262 (.262)	248 (.248)
(2)	10	14	30.5	58.5	224 (.224)	195 (.195)	187 (.187)
(3)	10	12	24	48.5	192 (.192)	153 (.153)	155 (.155)
(4)	10	10.5	24.5	48	168 (.168)	156 (.156)	153 (.153)
(5)	10	9.5	21	42	152 (.152)	134 (.134)	134 (.134)
(6)	10	3.5	7.5	15.5	56 (.056)	48 (.048)	49 (.049)
(7)	10	2	4.5	9	32 (.032)	29 (.029)	29 (.029)
(8)	10	2	4	8	32 (.032)	25 (.025)	25 (.025)

* Measured on RVT Instrument with U.L. Adapter.

Eight copolymers having a molar ratio of 1.5:1 AMPS/NNDMA were synthesized. The absolute molecular weights of these polymers were not determined. However, the samples were graded in decreasing order of molecular weight by viscosity using a 1000 parts per million concentration of copolymer

in water. The viscosities were measured on a Brookfield viscometer with "New UL Adapter" using "RVT factors" supplied by the manufacturer. Spindle speeds of 1, 2.5 and 5 RPM were used. The values obtained at 5 RPM were used for comparison of viscosities. The polymer solutions were prepared by diluting the stock solutions of the polymers obtained from the polymerization equipment to 1000 ppm. The solid contents of the stock solutions were previously estimated by precipitation of the polymers by acetone and weighing the dried polymer. The viscosities were expressed in centipoise at a given RPM of the spindle. This data is provided in Table IV.

The molecular weight of the copolymer is important for rheological reasons. As the molecular weight of the copolymer is increased, the viscosity of the cement slurry increases, finally reaching a point where it is essentially no longer pumpable. This point is reached when the Brookfield viscosity reading of a 1000 ppm solution of copolymer at 5 rpm of the U.L. Adapter S indle is somewhere above a reading of 250 centipoise (250 Pa s). Such reading corresponds approximately to a molecular weight of about 300,000. On the other hand, when under the same conditions, this Brookfield viscosity reading drops below a value of about 30 (which corresponds to a molecular weight of about 75,000), such copolymer's fluid loss characteristics diminish below an essentially effective level.

Although the proportionality between the solution viscosity and molecular weight of a macromolecule is an established fact, deviations occur with variation in copolymer composition, sequence length of the units, intermolecular and intramolecular interaction between the side chains and the overall conformation of the molecule. Rather simple and accurate results may be obtained when predicting the solution viscosity of a homopolymer of a given molecular weight if a calibration is available, however, the same prediction is more arbitrary in the case of copolymers such as the NNDMA/AMPS copolymers of the present invention which contain strongly ionizing $-SO_3H$ units as well as $-N(CH_3)_2$ groups which can be protonated under strongly acidic conditions. In other words, two samples of the copolymers of the same composition and molecular weight may have widely differing solution viscosities depending on sequence length of the component monomer units, which length is governed by the reaction conditions employed during polymerization.

The Samples (1), (2), (4), (5), (6) and (8) of Table IV were tested for fluid loss properties. Samples (1), (2), (4), (5) and (6) performed similarly in fresh water. Sample (8) did not provide good fluid loss properties in fresh water. Thus, the molecular weight ranges of the copolymers should be between about 75,000 and about 300,000.

Tests relating to WOC (waiting time which is defined as the time required for the slurry to obtain a compressive strength of 500psi (3.45 MPa) on cement and 24 hour compressive strengths were made with cement compositions containing copolymers of NNDMA/AMPS having mole ratios of 1:1.5 are provided in Table V.

Table V
Effects of Fluid Loss Additives on
Strength Development
Base slurry - Class H Cement + 46% Water

Additive	Mole Ratio	% Additive By Weight of Dry Cement	Temp (°F(°C))	Initial Set Time (hr:min)	WOC Time (hr:min)	24 Hour Compressive Strength (psi (MPa))
NNDMA/AMPS	1:1.5	0.6%	80(26.7)	9:25	14:57	940 (6.5)
NNDMA/AMPS	1:1.5	0.8%	80(26.7)	8:57	14:26	980 (6.8)
NNDMA/AMPS	1:1.5	0.6%	100(37.8)	7:01	10:12	1410 (9.7)
NNDMA/AMPS	1:1.5	0.8%	100(37.8)	6:49	10:30	1390 (9.6)
NNDMA/AMPS	1:1.5	0.6%	120(48.9)	3:58	6:10	2300 (15.9)
NNDMA/AMPS	1:1.5	0.8%	120(48.9)	4:24	7:06	2000 (13.8)
NNDMA/AMPS	1:1.5	0.6%	140(60)	3:11	5:07	2550 (17.6)
NNDMA/AMPS	1:1.5	0.8%	140(60)	3:40	6:10	2080 (14.3)

The preceding Tables I to V and related description relate to copolymers of NNDMA/AMPS and not to copolymer salts. The properties of the corresponding salts, however, are in general not very different from those of the copolymers. The sort of differences are illustrated by the results in Table VI. This Table shows rheological and fluid loss test results wherein the NNDMA/AMPS copolymer having a mole ratio of 1:1.5 is neutralised with several different bases. Slurries containing these copolymer salts were made which also

contained common salt in an amount of 18% by weight of water.

Table VI
Effects of Various Salts of a 1:1.5 Molar NMDMA/AMPS Copolymer
on Fluid Loss Performance at 125°F (52°C)

Base Slurry - Class H Cement + 46% water

Sample No.	Neutralizing Alkaline Agent	% Equivalent Copolymer Acid by Weight Cement	% NaCl by Weight Water	Halliburton Consistometer		Fluid Loss
				Rheology at 0 Min	Rheology at 20 Min	
1	None	0.6	0	6	9	34
2	None	0.8	18	8	9	114
3	NaOH	0.6	0	6	8	30
4	NaOH	0.8	18	6	9	226
5	KOH	0.6	0	7	9	32
6	KOH	0.8	18	6	10	203
7	NH ₄ OH	0.6	0	6	8	34
8	NH ₄ OH	0.8	18	6	9	135
9	Ca(OH) ₂	0.6	0	5	8	32
10	Ca(OH) ₂	0.8	18	6	8	122
11	Mg(OH) ₂	0.6	0	10	9	38
12	Mg(OH) ₂	0.8	18	7	9	48

The results in Table VI show that all the copolymer salts behave very similarly in 0% salt slurries. In 18% salt slurries, however, the performances of the copolymer salts varies. If the copolymer is neutralised with NaOH or KOH, the fluid loss is higher than that found with the unneutralised copolymer. When NH₄OH or Ca(OH)₂ is used, the salts give similar fluid loss response to the unneutralised form of the copolymer.

The $Mg(OH)_2$ neutralised form of the copolymer has a lower fluid loss than the unneutralised copolymer.

A further advantage of the neutralised salts of the copolymer is the ease of handling such materials. Salts of polymers and copolymers tend to be less hygroscopic which generally results in less lumping of the material during storage. Use of the salts will also eliminate the obvious hazards of handling acidic compounds.

Hence, a preferred fluid loss additive copolymer salt of NNDMA and AMPS has a mole ratio of about 1:4 to about 4:1 and a molecular weight of between 75,000 and about 300,000. When used in cement slurries containing appreciable amounts of common or other mineral salts, the most preferred fluid loss additive copolymer salt of NNDMA and AMPS has a mole ratio of about 1:1.5 respectively and a molecular weight between 150,000 and 250,000.

Claims

1. A cementing composition for use in oil, gas and water well cementing operations comprising water, hydraulic cement, and a copolymer salt, the copolymer being derived from N,N-dimethylacrylamide and 2-acrylamido-2-methyl propane sulfonic acid or an acid salt thereof, and having a mole ratio of N,N-dimethylacrylamide to 2-acrylamido-2-methyl propane sulfonic acid (or salt) from about 1:4 to about 4:1, and a molecular weight of about 75,000 to 300,000.
2. A composition according to claim 1, wherein the copolymer salt is present in an amount of from about 0.1% to about 1.5% by weight of cement.
3. A composition according to claim 1 or 2, wherein the water also contains up to about 18% common salt, by weight of water.
4. A composition of claim 1, 2 or 3, wherein the mole ratio of N,N-dimethylacrylamide to 2-acrylamido-2-methyl propane sulfonic acid in said copolymer is 1:1.5.
5. A composition according to any of claims 1 to 4, wherein said copolymer salt is formed by neutralisation of the acid copolymer.
6. A composition according to any of claims 1 to 4, wherein the copolymer salt is formed by copolymerisation of the N,N-dimethylacrylamide with a 2-acrylamido-2-methyl propane sulfonic acid salt.
7. A composition according to any of claims 1 to 6, wherein the salt contains ions of at least one of calcium, magnesium and ammonium.
8. A composition according to claim 1, wherein the molecular weight of said copolymer salt is between 150,000 and 250,000 and the mole ratio of N,N-dimethylacrylamide to 2-acrylamido-2-methyl propane sulfonic acid (or salt) is about 1:1.5.
9. A method of cementing a conduit in a borehole penetrating an earthen formation by introducing a cementing composition into the space between said conduit and said formation, wherein said cementing composition is as defined in any of claims 1 to 8.
10. The use of a composition as claimed in any of claims 1 to 8, for cementing a conduit in a borehole penetrating an earthen formation.

Revendications

1. Composition de cimentation destinée à être utilisée dans les opérations de cimentation des puits de pétrole, de gaz et d'eau, comprenant de l'eau, un ciment hydraulique et un sel de copolymère, le copolymère étant à base de N,N-diméthylacrylamide et d'acide 2-acrylamido-2-méthylpropanesulfonique ou d'un sel de celui-ci et présentant un rapport molaire N,N-diméthylacrylamide/acide 2-



The $\text{Mg}(\text{OH})_2$ neutralised form of the copolymer has a lower fluid loss than the unneutralised copolymer.

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1. A cementing composition for use in oil, gas and water well cementing operations comprising water, hydraulic cement, and a copolymer salt, the copolymer being derived from N,N-dimethylacrylamide and 2-acrylamido-2-methyl propane sulfonic acid or an acid salt thereof, and having a mole ratio of N,N-dimethylacrylamide to 2-acrylamido-2-methyl propane sulfonic acid (or salt) from about 1:4 to about 4:1, and a molecular weight of about 75,000 to 300,000.
2. A composition according to claim 1, wherein the copolymer salt is present in an amount of from about 0.1% to about 1.5% by weight of cement.
3. A composition according to claim 1 or 2, wherein the water also contains up to about 18% common salt, by weight of water.
4. A composition of claim 1, 2 or 3, wherein the mole ratio of N,N-dimethylacrylamide to 2-acrylamido-2-methyl propane sulfonic acid in said copolymer is 1:1.5.
5. A composition according to any of claims 1 to 4, wherein said copolymer salt is formed by neutralisation of the acid copolymer.
6. A composition according to any of claims 1 to 4, wherein the copolymer salt is formed by copolymerisation of the N,N-dimethylacrylamide with a 2-acrylamido-2-methyl propane sulfonic acid salt.
7. A composition according to any of claims 1 to 6, wherein the salt contains ions of at least one of calcium, magnesium and ammonium.
8. A composition according to claim 1, wherein the molecular weight of said copolymer salt is between 150,000 and 250,000 and the mole ratio of N,N-dimethylacrylamide to 2-acrylamido-2-methyl propane sulfonic acid (or salt) is about 1:1.5.
9. A method of cementing a conduit in a borehole penetrating an earthen formation by introducing a cementing composition into the space between said conduit and said formation, wherein said cementing composition is as defined in any of claims 1 to 8.
10. The use of a composition as claimed in any of claims 1 to 8, for cementing a conduit in a borehole penetrating an earthen formation.

Revendications

1. Composition de cimentation destinée à être utilisée dans les opérations de cimentation des puits de pétrole, de gaz et d'eau, comprenant de l'eau, un ciment hydraulique et un sel de copolymère, le copolymère étant à base de N,N-diméthylacrylamide et d'acide 2-acrylamido-2-méthylpropanesulfonique ou d'un sel de celui-ci et présentant un rapport molaire N,N-diméthylacrylamide/acide 2-



acrylamido-2-méthylpropanesulfonique (ou sel) d'environ 1:4 à environ 4:1, et une masse moléculaire d'environ 75000 à 300000.

2. Composition selon la revendication 1, dans laquelle le sel de copolymère est présent en une proportion d'environ 0,1 % à environ 1,5 % en poids du ciment.
3. Composition selon l'une des revendications 1 ou 2, dans laquelle l'eau renferme également jusqu'à environ 18 % de chlorure de sodium, par rapport au poids d'eau.
4. Composition selon l'une des revendications 1, 2 ou 3, dans laquelle le rapport molaire N,N-diméthylacrylamide/acide 2-acrylamido-2-méthylpropanesulfonique dans ledit copolymère est 1:1,5.
5. Composition selon l'une quelconque des revendications 1 à 4, dans laquelle le sel de copolymère est obtenu par neutralisation du copolymère acide.
6. Composition selon l'une quelconque des revendications 1 à 4, dans laquelle le sel de copolymère est obtenu par copolymérisation du N,N-diméthylacrylamide avec un sel de l'acide 2-acrylamido-2-méthylpropanesulfonique.
7. Composition selon l'une quelconque des revendications 1 à 6, dans laquelle le sel contient des ions d'au moins une des espèces calcium, magnésium et ammonium.
8. Composition selon la revendication 1, dans laquelle la masse moléculaire dudit sel de copolymère est comprise entre 150000 et 250000 et le rapport molaire N,N-diméthylacrylamide/acide 2-acrylamido-2-méthylpropanesulfonique (ou sel) est environ 1:1,5.
9. Procédé de cimentation d'une conduite dans un trou de forage pénétrant une formation terrestre, par introduction d'une composition de cimentation dans l'espace compris entre ladite conduite et ladite formation, procédé dans lequel ladite composition de cimentation est telle que définie dans l'une quelconque des revendications 1 à 8.
10. Utilisation d'une composition telle que revendiquée dans l'une quelconque des revendications 1 à 8, pour cimenter une conduite dans un trou de forage pénétrant une formation terrestre.

Ansprüche

1. Zementierungszusammensetzung zur Verwendung in Öl-, Gas- und Wasserbohrlochzementierungsarbeiten, enthaltend Wasser, hydraulischen Zement und ein Copolymersalz, dessen Copolymer von N,N-Dimethylacrylamid und 2-Acrylamido-2-methylpropanesulfonsäure oder deren Säuresalz abgeleitet ist und ein Molverhältnis von N,N-Dimethylacrylamid zu 2-Acrylamido-2-methylpropanesulfonsäure (oder deren Salz) von etwa 1 : 4 bis etwa 4 : 1 und ein Molekulargewicht von etwa 75 000 bis 300 000 hat.
2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Copolymersalz in einer Menge von etwa 0,1 Gew.-% bis etwa 1,5 Gew.-% bezogen auf das Gewicht des Zementes vorhanden ist.
3. Zusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Wasser bis zu etwa 18 Gew.-% gewöhnliches Salz enthält, bezogen auf das Gewicht des Wassers.
4. Zusammensetzung nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß das Molverhältnis von N,N-Dimethylacrylamid zu 2-Acrylamido-2-methylpropanesulfonsäure in dem Copolymer 1 : 1,5 beträgt.
5. Zusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das Copolymersalz durch Neutralisation des sauren Copolymeren gebildet ist.
6. Zusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das Copolymersalz durch Copolymerisation von N,N-Dimethylacrylamid und einem Salz der 2-Acrylamido-2-methylpropanesulfonsäure gebildet ist.



7. Zusammensetzung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das Salz Ionen von wenigstens einem von Calcium, Magnesium und Ammonium enthält.
8. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Molekulargewicht des Copolymeralsalzes zwischen 150 000 und 250 000 liegt und das Molverhältnis von N,N-Dimethylacrylamid zu 2-Acrylamido-2-methylpropansulfonsäure (oder deren Salz) etwa 1 : 1,5 beträgt.
9. Verfahren zum Zementieren einer Rohrleitung in einem Bohrloch, das eine Erdformation durchsetzt, bei dem eine Zementierungszusammensetzung in den Raum zwischen der Rohrleitung und der Formation eingebracht wird, gekennzeichnet durch eine Zementierungszusammensetzung nach einem der Ansprüche 1 bis 8.
10. Verwendung der Zusammensetzung nach einem der Ansprüche 1 bis 8 zur Zementierung einer Rohrleitung in einem Bohrloch, das eine Erdformation durchsetzt.