

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
12 February 2004 (12.02.2004)

PCT

(10) International Publication Number
WO 2004/013460 A1

(51) International Patent Classification⁷: **E21B 33/13**,
C09K 3/00

Aramco, Dhahran 31311 (SA). **NASR-EL-DIN, Hishan, A.** [CA/SA]; 539 Radhwa LN, DHA, Box 12237 Saudi Aramco, Dhahran 31311 (SA).

(21) International Application Number:
PCT/US2002/033482

(74) **Agent: CINAMON, Jay, S.**; Abelman, Frayne & Schwab, 150 E. 42nd Street, New York, NY 10017-5612 (US).

(22) International Filing Date: 21 October 2002 (21.10.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/211,182 2 August 2002 (02.08.2002) US

(81) **Designated States (national):** AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(63) **Related by continuation (CON) or continuation-in-part (CIP) to earlier application:**
US 10/211,182 (CON)
Filed on 2 August 2002 (02.08.2002)

(84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) **Applicants (for all designated States except US): SAUDI ARABIAN OIL COMPANY** [SA/SA]; P.O. Box 5000, Dhahran 31311 (SA). **ARAMCO SERVICES COMPANY** [US/US]; 9009 West Loop South, Houston, TX 77096 (US).

Published:
— with international search report

(72) **Inventors; and**

(75) **Inventors/Applicants (for US only): TAYLOR, Kevin,** C. [CA/SA]; 531 Safaniya Dr. DHA, Box 8745 Saudi

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) **Title:** THERMALLY RESPONSIVE AQUEOUS SILICATE MIXTURE

(57) **Abstract:** Sealing a zone in a subterranean well-formation is affected with an aqueous silicate solution containing an alkali metal silicate, at least one activator and a mixture of a chelating agent and a phosphonate. This composition greatly increases the divalent ion tolerance of the silicate gelling system.

WO 2004/013460 A1

THERMALLY RESPONSIVE AQUEOUS SILICATE MIXTURE

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a composition and method for greatly increasing the divalent ion tolerance of silicate gelling systems. More specifically, the method and composition of the present invention greatly increases the effectiveness of such gelling systems employed in petroleum reservoirs.

Description of the Prior Art

In oil field operations the production of excess quantities of water causes major economic loss due to decreased oil production, increased lifting costs, and increased separation and disposal costs associated with large amounts of produced water. Other production-related problems include increased corrosion rates and an increased tendency for emulsion and scale formation. Therefore, there is a critical need to reduce excessive water production.

Gelling polymers for water shutoff in petroleum reservoirs have been extensively evaluated. Based on such evaluations, the sodium silicate gel system has been identified as providing significant advantages for use in water shutoff. These advantages include significantly lower cost, better control over gel time, environmental safety, high temperature stability and stability of the gel components during shipment and storage. However, silicate

gels also have an important disadvantage. Specifically they are sensitive to high calcium and magnesium concentrations.

U.S. Patent No. 4,640,361 discloses that the addition of divalent ions, such as calcium or magnesium ion, to sodium silicate solutions will cause immediate gelation of the solution. However, this is highly undesirable in treating well formations, because many formations contain brines that are high in divalent ion concentration. As the sodium silicate solution comes in contact with the formation brine, premature gelling will result that prevents the sodium silicate solution from completely entering the formation.

Aqueous silicate solutions that are gelled or solidified with acid-producing activators are well-known and have been used in various applications, including grouting processes and in sealing and consolidation processes in subterranean well formations. Some examples of such applications are disclosed in U.S. Pat. Nos. 3,202,214; 3,375,872 and 3,435,899.

In alkaline solution, sodium silicate contains various molecular weight silica polymers. When sodium silicate is acidified to a pH value of less than 10.6, a three-dimensional network of silica polymers forms that creates a gel. A slight decrease in the pH greatly reduces gel time. As a result, gel times are difficult to control by the addition of acid.

Thermally responsive sodium silicate solutions employ an activator that results in gelation only after the solution is heated. Thermally responsive activators are disclosed in U.S. Pat. Nos. 4,293,440; 4,384,894; 4,640,361 and 5,320,171.

Gels have been used as blocking and diverting agents to treat injection and production wells for more than five decades (U.S. Pat. No. 2,402,588). Several factors determine the

success of a gel treatment in the field, including candidate selection, identification of the source water, proper choice of the gelling system and placement of the gel into the target zone.

U.S. Patent No. 4,137,087 employs alkali silicates, metal ions from the group Al^{3+} , Fe^{3+} , Cr^{3+} and Sn^{2+} , and ligands from the group consisting of ethylenediaminetetraacetate, diethylenetriaminepentaacetate, N-(hydroxyethyl)ethylenediaminetetraacetate, nitrilotriacetate, and 1-3-propanediaminetetraacetate, which cures the silicate solution by evaporation. There is no disclosure of temperature activated gelation in U.S. 4,137,087.

U.S. Patent No. 4,732,213 employs a chelating agent and a divalent ion such as calcium ion, to form a latent gelling agent. However, this patent is directed to colloidal silica gels, not sodium silicate gels. There are significant and distinct differences in the behavior of colloidal silica gels versus sodium silicate gels.

It is, accordingly, an object of the present invention to provide a composition and a method for gelling aqueous silicate compositions by using thermally responsive gelation activators which reduce the production of excess quantities of water, reduce corrosion rates and decrease the tendency for emulsion and scale formation. This gelling composition exhibits divalent ion tolerance.

SUMMARY OF THE INVENTION

The present invention contemplates the treatment of subterranean well formations to plug or seal a zone in said formation with an aqueous silicate solution containing an alkali metal silicate, at least one activator and a mixture of a chelating agent and a phosphonate to achieve the desired thermal responsiveness and produce the desired tolerance to divalent ions.

It has been found that the combined or joint use of a chelating agent and a phosphonate serves to increase the divalent ion tolerance of the silicate solutions. In other words, to inhibit the rate of gel formation or premature gelation, to a much greater extent than that which occurs when either chelating agents or phosphonates are used separately or individually.

By means of the composition and method of the present invention improved control over the gel time of silicate solutions is achieved in the presence of divalent ions. In addition, a high level of temperature stability is maintained, as well as stability of the gel components during shipment and storage.

DETAILED DESCRIPTION OF THE INVENTION

The silicates which can be employed in the composition and process of the present invention are the water-soluble silicates which form silicate polymer chains or which form a gel upon acidification. The preferred silicates are those of the alkali metals, particularly sodium, potassium, and combinations thereof. These silicates are commercially available as dry powders, or as concentrated aqueous solutions containing 38 to 55 parts solids per 100 parts of solution, and having a pH in the range of from about 10 to about 13.

In treating subterranean well formations in accordance with the present invention, the aqueous silicate solution is mixed with one or more activators to achieve the desired thermal responsiveness. Any of the activators disclosed in U.S. Patent Nos. 4,293,440, 4,384,894, 4,640,31 and 5,320,171, the specifications of which are incorporated herein by reference, can be employed. Exemplary activators are sodium trichloroacetate, trichloroacetic acid, ethyl trichloroacetate, ethylacetate, hydrochloric acid, sodium trichloroacetate, trichloroacetic acid, ethyl trichloroacetate, mannitol, glycerol, sucrose, lactose, dextrose, fructose, galactose, mannose, maltose, xylose, and urea, with urea being preferred.

The aqueous silicate solution must also contain a mixture of at least one chelating agent and at least one phosphonate to produce the desired tolerance to divalent ions to avoid premature gelation.

Exemplary of the chelating agents which can be employed in accordance with the present invention include propanediaminetetraacetate, diethylenetriaminepentaacetate, N-hydroxyethylenediamine triacetic acid, hydroxyethyliminodiacetic acid, nitrilotriacetate, and 1-3-propanediaminetetraacetate. A concentration of from about 0.5% to about 3.0%, by weight, of chelating agent has been found to be effective in the present process.

Exemplary of the phosphonates which can be employed in conjunction with the chelating agents are sodium phosphonate, phosphonic acid, diethylenetriamine pentamethylene phosphonic acid, methylenephosphonate, as well as their derivatives.

A phosphonate concentration of about 40ppm to about 200ppm has been found to be effective in the process of the present invention.

In accordance with the composition and process of the present invention, gelation occurs at a temperature between about 100°F to about 350°F, preferably between about 120°F to about 200°F.

The following examples will serve to more comprehensively illustrate the principles of the invention, but are not intended to limit its scope.

Example 1

In all of the following examples, 5 mL of a sodium silicate solution (containing 9 wt% sodium silicate and 3.6 wt% urea) was added to a series of screw cap test tubes. The test tube was stirred using a vortex mixer and a calculated volume of divalent ion was added as a 4 g/L solution. Increasing amounts of a divalent ion, either calcium or magnesium ion were added to the test tube series. The samples were heated to 65°C for one hour, allowed to cool, and their appearance was recorded. These examples demonstrate the concentration of divalent ion at which precipitation begins to occur in a sodium silicate solution.

Table 1. Divalent Ion Sensitivity of Calcium Silicate Solutions

Divalent Ion	Concentration Required to Cause Precipitation
Calcium Ion	80 mg/L
Magnesium Ion	225 mg/L

The results set forth in Table 1 above demonstrate that sodium silicate solutions react at low concentrations of calcium and magnesium ion to form a precipitate.

Example 2

The procedure of Example 1 was followed. In addition, however, increasing concentrations of nitrilotriacetic acid trisodium salt monohydrate (NTA) were employed. The results obtained are set forth in Table 2.

Table 2. Divalent Ion Sensitivity of Calcium Silicate Solutions with NTA

NTA Concentration, wt%	Divalent Ion Concentration Required to Cause Precipitation	
	Calcium	Magnesium
0.5	500	-
1.0	670	364
2.0	800	-
3.0	1330	670

It can be seen from Table 2 that NTA increases the tolerance of sodium silicate to both calcium and magnesium ions; as the NTA concentration increases, the divalent ion tolerance also increases.

Example 3

The procedure of Example 1 was followed. In addition, however, increasing concentrations of ethylenediamine tetraacetic acid tetrasodium salt (EDTA) were employed. The results obtained are set forth in Table 3.

Table 3. Divalent Ion Sensitivity of Calcium Silicate Solutions with EDTA

EDTA Concentration, wt%	Divalent Ion Concentration Required to Cause Precipitation	
	Calcium	Magnesium
0.5	552 mg/L	-
1.0	800 mg/L	360
2.0	923 mg/L	-
3.0	More than 1600 mg/L	923

It can be seen from Table 3 that EDTA increases the tolerance of sodium silicate to both calcium and magnesium ions, and is more effective than NTA on an equivalent weight basis.

Example 4

The procedure of Example 1 was followed, however, increasing concentrations of sodium phosphonate were employed. The results obtained are set forth in Table 4.

Table 4. Divalent Ion Sensitivity of Calcium Silicate Solutions with Sodium Phosphonate

Sodium Phosphonate Concentration ppm	Divalent Ion Concentration Required to Cause Precipitation	
	Calcium	Magnesium
40	80 mg/L	225 mg/L
100	80 mg/L	365 mg/L
200	365 mg/L	-

It can be seen from Table 4 that sodium phosphonate shows a small increase in divalent ion tolerance at concentrations above 100 ppm.

Example 5

The procedure of Example 1 was followed, but a combination of sodium phosphonate and EDTA was employed. The following results were obtained.

EDTA (wt%)/Sodium Phosphonate (ppm)	Divalent Ion Concentration Required to Cause Precipitation	
	Calcium	Magnesium
0.5/100	610 mg/L	491 mg/L
1.0/40	920 mg/L	552 mg/L

It can be seen from Table 5 that EDTA and sodium phosphonate in combination show improved results over EDTA alone. (Compare Table 3.) The addition of sodium phosphonate at low concentrations significantly improves the divalent ion tolerance of sodium silicate solutions. Sodium phosphonate alone at 40 ppm did not improve divalent ion tolerance, but when added to EDTA resulted in a significant improvement.

Example 6

The procedure of Example 1 was followed, but using a combination of sodium phosphonate and NTA. The results obtained are set forth in Table 6

Table 6. Divalent Ion Sensitivity of Calcium Silicate Solutions with NTA and Sodium Phosphonate

NTA (wt%)/Sodium Phosphonate (ppm)	Divalent Ion Concentration Required to Cause Precipitation	
	Calcium	Magnesium
0.5/40	491 mg/L	610 mg/L
1.0/40	970 mg/L	428 mg/L

It can be seen from Table 6 that NTA and sodium phosphonate in combination show improved results over NTA alone. (Compare Table 4). The addition of sodium phosphonate at low concentrations significantly improves the divalent ion tolerance of sodium silicate solutions. Sodium phosphonate alone at 40 ppm did not improve divalent ion tolerance, but when added to NTA resulted in a significant improvement.

The invention is not limited to the above-described specific embodiments thereof. It should be understood that the detail involved in the description of these embodiments is presented for illustrative purposes only, and that reasonable variations and modifications, which will be apparent to those skilled in the art, can be made without departing from the spirit and scope thereof.

What is claimed is:

1. A composition for increasing the gel formation tolerance of aqueous alkali metal silicate solutions to divalent ions present in subterranean formations, which comprises:
 - (a) an aqueous alkali metal silicate solution;
 - (b) a thermally responsive gelation activator; and
 - (c) a mixture of a phosphonate and a chelating agent.
2. The composition of claim 1, wherein the alkali metal silicate is sodium silicate.
3. The composition of claim 1, wherein the phosphonate is selected from the group consisting of sodium phosphonate, phosphonic acid, diethylenetriamine pentamethylene phosphonic acid, methylenephosphonate and their derivatives.
4. The composition of claim 1, wherein the concentration of the phosphonate is about 40 to about 200 ppm.
5. The composition of claim 1, wherein the chelating agent is selected from the group consisting of ethylenediamine tetraacetic acid, propanediamine tetraacetate, diethyltriamine pentaacetate, N-hydroxyethylenediamine triacetate, hydroxyethyliminodiacetic acid, nitrilotriacetate, and 1,3-propanediaminetetraacetate.
6. The composition of claim 1, wherein the concentration of the chelating agent is about 0.5 to 3.0%, by weight.
7. The composition of claim 1, wherein gelation occurs at a temperature of about 100°F to about 350°F.

8. The composition of claim 7, wherein gelation occurs at a temperature of about 120°F to about 200°F.

9. A method of plugging or sealing a zone in a subterranean formation with an aqueous alkali silicate solution which has an increased gel formation tolerance to divalent ions present in said formation, which comprises:

- (a) introducing into said zone an aqueous alkali metal silicate composition comprising,
 - (i) an aqueous alkali metal silicate solution,
 - (ii) a thermally responsive gelation activator, and
 - (iii) a mixture of a phosphonate and a chelating agent;
- (b) activating said gelation activator in response to a thermal change in said composition within said formation whereby said silicate composition forms a gel in said zone.

10. The method of claim 9, wherein the alkali metal silicate is sodium silicate.

11. The method of claim 9, wherein the phosphonate is selected from the group consisting of sodium phosphonate, phosphonic acid, diethylenetriamine pentamethylene phosphonic acid, methylenephosphonate and their derivatives.

12. The method of claim 9, wherein the concentration of the phosphonate is about 40 to about 200 ppm.

13. The method of claim 9, wherein the chelating agent is selected from the group consisting of ethylenediamine tetraacetic acid, propanediamine tetraacetate, diethyltri-amine

pentaacetate, N-hydroxyethylenediamine triacetate, hydroxyethyliminodiacetic acid, nitrilotriacetate, and 1,3-propanediaminetetraacetate.

14. The method of claim 9, wherein the concentration of the chelating agent is about 0.5 to 3.0%, by weight.

15. The method of claim 9, wherein gelation occurs at a temperature of about 100°F to about 350°F.

16. The method of claim 15, wherein gelation occurs at a temperature of about 120°F to about 200°F.

saudiar\81701tay.apl

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/33482

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : E21B 33/13; C09K 3/00

US CL : 507/237, 241; 166/293

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 507/237, 241; 166/293

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,529,125 A (DI LULLO ARIAS et al) 25 June 1996 (25.06.1996) , see Table 7 and column 3, lines 18-29.	1-3
Y	US 4,676,832 A (CHILDS et al.) 30 June 1987 (30.06.1987), see Table X.	1-16

☐

Further documents are listed in the continuation of Box C.

☐

See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

23 January 2003 (23.01.2003)

Date of mailing of the international search report

20 FEB 2003

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703)305-3230

Authorized officer
Philip C. Tucker

Telephone No. 703-308-0651

INTERNATIONAL SEARCH REPORT

PCT/US02/33482

Continuation of B. FIELDS SEARCHED Item 3:

EAST

search terms: silicate, phosphonate, subterranean, sodium silicate, potassium silicate, alkali metal silicate, chelating or chelant.