Available online at www.elixirpublishers.com (Elixir International Journal)

### **Applied Chemistry**





# Sodium silicate cement squeeze in massive salt formations: chemistry and chemical evolutions

M.D. Garba<sup>1, 2</sup>

<sup>1</sup>Department of Pure and Industrial chemistry, Bayero University Kano, P.M.B 3011, Kano Nigeria <sup>2</sup>Oil and Gas Chemistry (MSc), University of Aberdeen, AB24 1WU, Aberdeen, UK

#### ARTICLE INFO

Article history: Received: 31 August 2012; Received in revised form: 30 September 2012; Accepted: 6 October 2012;

#### Keywords

Sodium silicate, Cement, Squeeze, Brine flow, Zechstein formation, Gelation.

#### ABSTRACT

Setting a conventional cement plug is nearly unsuccessful when there is any wellbore flow especially for the zechstein formations. As such, the used of sodium silicate remain the common option. The silicate polymerization and gelation has been used in well formation to plug holes and reduce the catastrophic flow which cause a lot of production looses. This is usually encountered during drilling rocks zone producing large amount of water or brine. This could result in large volume of the drilling fluid lost into the formation and consequently reduce the effectiveness of the drilling operations. A well designed silicate/cement material forms an impermeable plug and reduces the adverse of the flow also the in-situ gelation of the process is better understood when the chemistry of the process and the chemical evolution of the brine formation is given due consideration.

© 2012 Elixir All rights reserved.

#### Introduction

Wellbore flow is one of the most common problems encountered in most of maturing oilfields due to excessive outbreak of production water, gases migrations, sands influx, and or brine influx due to zechstein formations. Although the term brine should actually be preserved to describe normal saline formation water, it has been common practice in the drilling community to describe high-pressure flow of salts as 'brine flows'. Brine flows (or brine pockets) are interpreted to be volumes of porous rock salt, with the porosity filled by brine potentially at lithostatic pressure.

Brine flows are occasionally encountered in the Zechstein Group and can occur in the Zechstein halite formations (Z4, Z3, and Z2) and their pressure can be as high as lithostatic. The composition of the brines is  $MgCl_2$ -rich and for that reason brine flows can be detrimental to cementation as the risk of "flash-setting" increases. At the moment their occurrence is still not fully understood, neither are they visible on seismic and, therefore, currently impossible to predict. It is observed in the field that brine flows can occur no matter what adjustments are made to mud weight.

The process of design and placement of effective cementing work is of very critical to the profitable success of every oil and gas production wells. Quality cementing jobs not only provide necessary protection, strengthening, and stability of the well casing, but also provide a technology to seal off pipe leaks and also protect the pipe. Conventional cement has although been reported to have encountered a lot of unsuccessful operations for brine formations (Marca, 1990).

In oil and gas reservoirs, brine flow is a serious well given attention issue. Many variety of technology have been used to control brine flow by the oil industries. Field result studies have consistently shown satisfactory achievement with sodium silicate base system. (Liu et al, 2006; Samari, et al., 1998). An

Tele: E-mail addresses: mustcapture@yahoo.com © 2012 Elixir All rights reserved effective and appreciable measures taken in reducing the wellbore flow is by taking advantage of the sodium silicate gelation and polymerization reaction. Silicates have the stability to polymerize and form gel, or plugs. This is achieved with applications of other chemicals, based on their plug forming ability with silicate and stability of the plug at various temperatures (Stephen et al., 2005).

The polymerization of silicates will continue to be popular methods for solving problems in oil and gas industries during drilling. Over 500 production wells had been treated using this method to reduce the water/oil ratio produce (Rensvold et al., 1975), other include water flooding, enhance oil recovery projects and improving economic of well production by increasing oil productions.

Possibly, brine contaminate undesirably the fresh water, different fluid flow in the well can be control and design by injecting silicate solution into the open flow channels in the cement sheath. Rapid gellation occurs to plug off these flow channels.

#### Sodium silicate chemistry

Sodium silicate (Na<sub>2</sub>O.SiO<sub>2</sub>) is a generic term just like clay, but it is a man-made substance. It is chemically inorganic colloidal compound and popularly known also as sodium metasilicate, soluble glass, liquid/ and or water glass. Sodium silicate is a white or grey white powder, soluble in solvent such as water or alkaline, but insoluble in acid and alcohol. Sodium silicate is also available in different viscous liquid depending on silica to soda ratio. Industrially; sodium silicate has many uses. They are use as abrasive, asbestos, adhesive glass. Cementing and protective coating are also some of it is applications. Sodium silicate is also getting to be used with other compound for better workability; carbon dioxide is use as a sodium silicate hardener for excellent binder.

#### **Preparation of Sodium Silicate**

Sodium silicate is prepared as a molten glass; this is achieved by fluxing purified quartz sand with alkali carbonate.

SiO<sub>2</sub> + Na<sub>2</sub>CO<sub>3</sub>  $\longrightarrow$  Na<sub>2</sub>O.SiO<sub>2</sub> + CO<sub>2</sub> Crushed or granular silica is crushed in an open furnace with soda at a temperature of about 1371°C (2500°F).

Sodium silicate is state of matter ranges from soluble liquid (polysilicic acid), solid hydrate and silica gels. Solubility of the silicate is strongly depending on the ratio of silica to alkali given as weight ratio of SiO<sub>2</sub> to Na<sub>2</sub>O. E.g. A weight ratio of 3.22 parts SiO<sub>2</sub> and 1 part Na<sub>2</sub>O is referred to as 3.22 silicate ratio (i.e.  $SiO_2:Na_2O = 3.22:1$ ).

The composition of sodium silicate is most conveniently indicated referring to the silicon and sodium oxides composition even without precise knowledge of the inter-element bonding or implying that the oxide exist in the system and/or the ratio is determined by any stoichiometrical boundaries (Owusu 1982).

#### **Properties of Sodium Silicate**

It is a colloidal Newtonian liquid until it viscosity rises due to neutralization of the SiO2-Na<sub>2</sub>O bond, or overcomes by chemical reactions; the two components became independent of each other.

When SiO2 tend to precipitate by polymerization in form of silici acid (H2SiO4) high percentage of Na2O remains in the slution forming NaOH. Therefore, in sodium silicate solution, the positive Na<sup>+</sup> cation and the negative SiO<sub>2</sub><sup>2-</sup> anion as well as the negative ionic micelle are the cause of the colloidal silica.

Sodium silicate provides deformability necessary for adhesive properties. This is achieved considering micelles stability due to adsorbed  $Na^+$ . In settings or reactivity, they are been replaced by hydrogen bonds or by silica which react with the substrate.

The characteristics are less pronounced at high viscosities (Houwink 1965) and its rate of wetting strongly depends on dilution silicate ratio, viscosity and alkalinity. Aqueous soluble silicate wet readily on most surface. These include organic material, rocks and /or sands.

Sodium silicates act as binders considering its ability to form a precipitated gel and silicic acid. This is due to its ability to form cohesive substance consisting of countless individual colloidal particles.

#### Silicate Structure

The  $SiO_2$  molecular bonding is based on the tetrahedral structure group (SiO<sub>4</sub>), bonding together by complex polymerization into chain network.



Fig. 1. Silicate tetrahedral structure

This indicates that silicate needs to acquire four electrons to have an octet valance shell configuration. This may be provided by metal atoms which are present in the silicate cations. It is possible for these tetrahedral groups to cross linked by their corner, sharing oxygen atoms forming an endless structure and extend continuous through a given crystal and consequently a giant molecule (figure 2).



Fig.2. crosslink endless structure of tetrahedral silicate structure

#### **Reactivity of Sodium Silicate**

The silicate as a simple system involve problem of whether or not soluble in water to for sols. Silicate hydrolysed to form monomeric silicate acid in ortho form  $(H_4SiO_4)$  or metasilicic acid  $(H_2SiO_3)$ , but there are no direct possibilities of obtaining either monomeric or Meta silicic acid.

Eitel, 1964 report that polymerization of silicate set-in automatically even at low temperature and or optimum temperature for better stability of a low molecular weight silicic acid form. Hydrolysis of silicate depends strongly on pH and as such a precise way for understanding automatic condensation process of the silicate. Particle of sodium silicate of its sols carry negative electric charge in alkaline, neutral and weak acidic solution, while positively charge in strong acidic solution (a reversal characteristic as a result of environmental medium). Meanwhile, (Debye and Nauman 1949), reveal that a higher ratio SiO<sub>2</sub>:Na<sub>2</sub>O ratio (> 3.0:1) gives a higher state of polymerization of silica.

## Condensation of Polymerization of Polysilicic Acid in Sodium Silicate Solution

Condensation polymerizations occur whenever the positive and negative ion contain the silicone combines and release water by adsorption. All  $\epsilon$  + mental data available showed that a colloidal silicic acid gel is formed by condensation reaction. Hurd, 1938 report that; a monomer silicate which is unstable combined with another monomer to give a dimer. The dimer then joins with another monomer to form a trimer. Without the showing of ONa- group, the reaction can be presented as follow:-



Fig. 3. combination of two mono-silicic acids to produce a dimmer



Fig. 4. combination of a mono and dimmer silicic acid to produce trimer

Once the OH<sup>-</sup> group are replace by  $O^{2-}$  ion with higher polarizability, it condense with final generesis to a silica hydrogel shorten the Si<sup>4+</sup>- Si<sup>4+</sup> distance. However, once the polymerization process continuous and achieved to an extend that the solution of silicic acid has formed long chain through development of gel, head build-up tension within the chain and consequently imparts rigidity to gel (Owusu 1982). Heymann, 1935 revealed sodium silicate is in equilibrium with silicic acid, polysilicic acid, and the gel. This can be expressed as follows:



Fig. 5. illustration of sodium silicate in equilibrium to silicic acid in gel formations

#### Factor Affecting Gelation and Polymerization of Sodium **Silicate Solution**

1)Amount of sodium water: The less the water, the faster the gelation and consequently the bonded become extremely weak and friable

2)pH of the solution: Polymerizations occur less rapidly at high pH of 8 and above (basic region) and occur rapidly faster at a lower pH (acidic region).

3)SiO<sub>2</sub>/Na<sub>2</sub>O ratio: Polymerization is obtained faster with higher ration of SiO<sub>2</sub>/Na<sub>2</sub>O of about 3.3 (i.e. 3.3: 1.0) (Iler 1953)

4) Temperature (dehydration process): Change of sodium silicate phase by dehydration from liquid to solid by loss water.

5)Foreign ions: Presence of ions such as Cl<sup>-</sup> and F<sup>-</sup> delayed the gelation process, participating in the solubility of silica. If F is present; it can undergo true chemical reaction and form (SiF6)<sup>2-</sup> complex anion considerably reducing the polymerization. While Cl and Br were found to accelerate the process due to their catalytic effect (Eitel 1964).

#### Sodium Silicate Curing Mechanism as a Binder

Hydrated sodium silicate written as Na<sub>2</sub>(H<sub>2</sub>SiO<sub>4</sub>) . 8H<sub>2</sub>O. Dissociated as follow:-

 $Na_2(H_2SiO_4)$ .  $8H_2O$  + water  $2Na^+$  +  $H_2SiO_4^{2-}$  +  $H_2O$ Greenberg and Sinclair, 1955 report that, the silicic acid  $H_2SiO_4^{2-}$  have low ionization constant (K1 = 1x10-9.8, K2 = 1x10-1.4) and therefore hydrolyses in two steps in dilute basic solution (pH 8-9).



#### Fig. 6. Hydrolysis of silicic acid

When hydrated crystals of sodium silicate are expose to CO2, its form colloidal silicic acid and gelation begins in-situ due to increase in viscosity. Fluid sodium silicate hardens as adhesive simply by loss water or by saturated solid silicate by liquid or solid reagent or by lowering temperature. Thus, sodium silicate bond can be cured by either pH change, physical dehydration or by combination of both.

#### pH Change in Binder Cured with CO<sub>2</sub>

CO<sub>2</sub> gas can react with Na<sub>2</sub>O.SiO<sub>2</sub> to produce mono-silicic acid decreasing the pH of the region and enhancing gel formations  $Na_2O.2SiO_2 + CO_2 + 4H_2O \longrightarrow 2Si(OH)_4 + Na_2CO_3$ 

Ionically;

 $\begin{array}{c} Na_{2}O.2SiO_{2}+5H_{2}O & 2Na^{+}+2Si(OH)_{4}+2(OH)^{-}\\ CO_{2}+H_{2} & 2H^{+}+CO_{3}^{2-} \mbox{ (carbonic acid)}\\ OH^{-} \mbox{ and } H^{+} \mbox{ combine to give water reducing the pH of} \end{array}$ 

Na<sub>2</sub>O.2SiO<sub>2</sub> solution.

$$H^{-} H^{+} H^{+} H^{-} H^{-$$

Importantly;

 $Na_2O.2SiO_2 + H_2O + CO_2 \longrightarrow Na_2CO_3 + (SiO_2.H_2O)$ 

The hydrated silica gel further loses water until its strength by the process of syneresis.

The Na<sup>+</sup> and  $CO_3^{2^-}$  ion presence in the reaction mechanism can be replaced by foreign ions and therefore, may consequently affect the polymerization reaction of the silicate.

#### **Binder Cured by Physical Dehydration**

This take place when there is sufficient heat to pull out the water content of the silicate solution. Thus, physical dehydration of sodium silicate can be achieved by using conventional heat energy, exposure to microwave energy, or exothermic reaction from organic or inorganic compounds. The physical dehydration of sodium silicate may be described by the ionic equation as follows:-

Na<sub>2</sub>O.SiO<sub>2</sub> + H<sub>2</sub>  

$$Dehydration \\ Hydration$$
 $(Glasssy-H_2O)$ 
 $Hydration$ 

Sodium silicate dehydrations and CO<sub>2</sub> reactions



#### Fig.7. reaction of sodium silicate solution with CO2



Fig. 8. Sodium silicate solution dehydration reaction

The Si-O-Si linkage called "siloxane" is the bond that gives rigidity to the bonded material and is a far stronger bond. The water loss increases, as the polymerization and gel formation occur. As such, the faster the rate of water loss, the faster the syneresis process takes place.

Gel formation can be summarized from sodium silicate solution using ternary phase diagram at room temperature (fig. 9). The phase diagram shows the stable form of sodium silicate to exist at a silica/soda weight ratio range from 2:1 to 3.75:1. The silica with high silica/soda ratio reacts faster. The phase also shows the transition of phases of silicate usually from liquid to viscous liquid to semi-solid and finally to dehydrated liquid accelerated by heating.



Fig. 9. sodium silicate solution ternary phase diagram (Owusu 1982)

#### Hydration Reaction of Cement and Sodium Silicate

Hydration reaction of cement with alkali activator such as sodium silicate is attributed to the production of alkali solution based paste. However, as a result the paste will set within 15 Minute (Yang et al. 2008). Consequently, it will cause a quick workability loss of the cement constituting major obstacles for its practical applications. In addition, the sodium hydroxide produce from the hydration reaction requires great caution. The quick setting of this cement as well as risk handling problem need to be solve, in order to improve its usage as a construction material.

In preparation reaction of sodium silicate/cement, the alkali quality coefficient combining the exact amount of material constituting the cement material is very important and also the ratio of the sodium silicate to be used should be given proper considerations.

The reaction of sodium silicate in the cement slurry solution is very influential by the amount of Na<sub>2</sub>O to the source material ratio by weight. Thus, Na<sub>2</sub>O to the source material should be consider as a variable to determine the additional amount of sodium silicate require in designing the cement slurry.

In the cement silicate system, there is tendency that the silicic acid provides the initial stability and the sodium silica gel in subsequent reactions by the sodium or potassium alkali present in the cement. This could also be derived from the alkali salt influx in excess of those needed to form the initial gel.

Sodium silicate served as a rapid setting additive to cement material (Houlsby 1990). Sodium silicates are chemically non corrosive, when added to cement in small quantity quickly causes a gel. The gel time strongly depends on the amount and ratio type of the sodium silicate used. Precisely, the higher the sodium silicate in the cement the faster the cement set.

The effective concentration of sodium silicate varies with concentration of the sodium silicate to the content of the cement. About 20% of calcium hydroxide is obtained of the weight cement used and the molar ratio less than one (Lea, 1979). The concentration of the Na<sup>+</sup> ion in the cement solution make it more viscous by ion exchange reaction between the Na<sup>+</sup> of the sodium silicate and the Ca<sup>2+</sup> of the cement. The gel strength formed is increased because the solubility of calcium oxide is increased by NaOH, while the solubility of the NaOH is increased by the water molecule.

Calcium hydroxide is produce by first hydration of cement. Therefore, when the dilute sodium silicate  $(Na_2SiO_3)$  mixed with the cement as the principal ingredient;  $Ca(OH)_2$  combine with the silicate ion  $(SiO_4^{-4})$ . Silicate-cement gel is formed. The formation mechanism can be illustrated as follow:-

$$Na_2SiO_3 + Ca(OH)_2 \longrightarrow CaSiO_3 + 2NaOH$$
$$Na_2SiO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2NaOH$$

 $Na_2SiO_3 + CaSO_4 \longrightarrow CaSiO_3 + Na_2SO_4$ This gave a tentative conclusion to creation of double layer and ion exchange occur between the silicate ions of sodium silicate and the calcium ions of the cement forming the calcium silicate hydrate gel (fig 10).



Fig. 30. Illustration of ion exchange sodium-silicate cement gel formation (Chun et al., 2008)

Most importantly, acid base reaction occur, for example Ca(OH)2 and SiO2 do not react in powdered form but prone to react in liquid due to the presence of Ca(OH)2 dissolving appreciably and increase the alkalinity of the solution sufficient to promote hydrolysis of silica. This causes the reaction of the Ca<sup>2+</sup> and the silica ion in the alkaline solution to rapidly occur, precipitating calcium silicate hydrate. Though, Presence of these calcium and silica ions does not normally necessitate their reaction to take place especially for neutral pH. Therefore, they do not react even with presence of the dissolve aqueous Ca<sup>2+</sup> and Mg<sup>2+</sup>. Consequently, pH can be expected to influence gelling mechanism. Charge ion density associated with hydrolytic dissociation with an increase pH effect which polarises metal ion oxygen M-O and weakens the water bonding O-H until dissociation occurs, releasing hydrogen ions.



Fig. 41. Dissociation caused by polarization of metal ion to release hydrogen ion

calcium; due to it is charge density provide M-O bonding stronger than that of water molecule on the Ca2+ ion and at significant pH offer precipitation of calcium silicate hydrate. Due to the high density of Ca2+; it also contributes to the stabilization of solid precipitate. Thus, precipitation of C-A-S-H gel can also begin at low Ca/Si ratio as shown below:



As  $C_3A$  also one of the principal component of the cement, due to that the cement suspension tend to produce CA or  $CA_2$  which react with Na2.SiO<sub>2</sub> and led to the formation of sodium calcium silicate hydrate

CaO.Al<sub>2</sub>O<sub>3</sub>+ Na<sub>2</sub>O.SiO2  $\longrightarrow$  [Na<sub>2</sub>Ca<sub>2</sub>Si<sub>2</sub>O.H<sub>2</sub>O] This converts the cement into a well crystallized compound, reflecting increases in the density of the cement as well as lowering the porosity of the cement matrix (Sugama, Carciello 1996). The silicate also react with [3Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>] present in the cement solution to yield a dense product which is an intermediate that enhance the degree of crosslinkng between the cement matrix and also improve the cement interfacial bond (Sugama, Carciello 1996).

[3Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>] + Na<sub>2</sub>SiO<sub>3</sub> → [NaAlSi<sub>2</sub>O<sub>6</sub>.H<sub>2</sub>O] Sodium silicate gel formation and gel strength

The pH has quite significant impact on gel formation of silica, at high pH (basic region) dimmer species dominate the environment, but when the pH is reduced the silicate will react to form gel through polymerization. Thus, to initiate gel formation, the pH is reduced to pH value below 11; illustration for the step development of the gel formation can be described in (fig.12). This can be seen as polymerization of monomer to form polymer followed by growth of particles and finally linking of the growing particle to form a big polymer chain forming a gel.



#### Fig. 52. illustration for the step development of gel formation (Krumrine & Boyce, 1985)

#### Effect of Gelation Time on Salinity and Divalent Ions

It is very important to determine and investigate the effect of salinity on the gelation time of an applying field for successful job operations. Formation water is a kind of water usually rich in metal ions such as  $Na^+$  and  $Ca^{2+}$  (concentrations depends on the formation environment) and this will have effect on gelation time.

This might sometimes cause the precipitation of calcium and/or magnesium silicate during the operation and consequently leading to unsuccessful of the operation. If the concentration of the metal ions (such as Na<sup>+</sup> and Ca<sup>2+</sup>) is too high in the treated formation, a need for preflushe with very low salinity water will first be require before any operation. A preflushe should be well designed for operation in order to significantly reduce the effect of the salinity on the gelation time. The effect of each ion present in the formation on the gelation time should be determine followed by combination of all the ions tend to be present for a good and precise mechanism of reaction.

#### **Gelation Time Control**

Gelation time is mostly control by varying the initial preparation pH and the amount of salt added (Jurinak, et al., 1989). In field treatment, sodium silicate gel formation is achieved by either the use of an internal or external activator. The internal activator works by decomposing itself into species that can initiate gelation. This internal activator are the type of organic, and/or ammonium salt (Krumrine & Boyce, 1985). The external activator works by precipitating silicates when mixed with the sodium silicates which are of the type calcium or magnesium chlorides.

Solution pH has most significant effect and therefore influences gel time of the sol sodium silicate. Sodium is a preferred counter ion, forming resonating gel with reproducible gel. Decrease in gel time with increase salinity is due to an increase charge shielding by the well hydrated, weakly charged Na+ ion. This allow the colloidal silica sol particles to approach one another closely enough to form silo-xane bones that form bridge between the particle

Fig shows the result of experiment conducted on sol silica to see the effect of pH on gelation time. This reveal that gel time minimum occurred in pH range of 6-7, but the range time of the gel that can be obtained is extensive. 5 wt% of sol silica gives a gel time ranges from as little as 20 min to more than 49 days in pH range of 5-9.5 (Jurinak, et al., 1989).



Fig. 63. Silica sol gel time data (Jurinak, et al., 1989) Squeeze cementing

Squeeze cementing has a long been an oil-well common operations. Numerous squeeze jobs are performed daily under different variety problems of down-hole conditions.

Squeeze cementing is the process by which cement slurry is force under pressure through holes or splits in the casing or wellbore annular space. In the process, the solid particle content of the slurry tends to filter out on the formation face while the cement aqueous filtrate enters into the formation matrix. Squeeze job can properly be designed to cause filter cakes that can be used to fill openings between formations and casing (fracture of leaks). The cakes form a nearly impenetrable solid for proper curing (Marca, 1990). The cement solids developed a filter cake on the fracture face and/or bridge the fracture (Marca, 1990).

Large volume of cement are pumped into fracture openings and propagated by high pressure and high pump rate. High final pressure, often regard as an indication of success occurs at the end of the pumping time. Rarely, dehydration of slurry may also occur into the perforations or even in the casing and/or diversion of the cement to un-cemented voids or plugged may also be accomplished (Schlumberger, 1984). Increase in pressure may also propagate fracture rather than diverting the cement to the existing plugged channels. Good knowledge and design of cement squeezing programme provide greater production efficiency, improve the success ratio, and lower the operation cost.

#### Why Squeeze Cementing?

Squeeze cementing has been a remedial option in oil and gas operations, it has many applications during both the drilling and the completion phase's operations as well as during productions. Its render a good remedy for wellbore flow cases and leaks as well as setting plugs for depleted oil reservoirs especially when there is a seismic tendency for future production of the reservoir. The most common squeeze cementing applications are as follows:-

Repairing of primary cementing jobs. 1)

Primary cementing jobs may fail due to cement by passing the mud (channelling) or as a result of insufficient cement height in the annulus. The poor primary cementations are usually the cause of expensive work over jobs. The by-passing of cement by the mud may cause channels which may be a potential source of problems during the production life of the well (Schlumberger, 1984). Example; communication between zones in a well, due to usual reservoir geological stress on formations (fig. 14) and perforations between top and bottom intervals occur due to unsuccessful primary cementing job (fig. 15).



Fig. 74. illustration for the communication of zone in a well (Schlumberger, 1984) (Schlumberger, 1984)



#### Fig. 85. Perforations between top and bottom intervals

2) Elimination of water intrusion and reduction of gas/oil ratio. As a well oil zone becomes depleted mostly in an ageing well, water or gas intrusion into the oil zone may occur. Squeeze cementing is usually often used to plug off all the perforation in both the water/gas and oil zone and then re-perforate in a shorter producing interval to avoid production of water/gas (fig. 16).



#### Fig. 96. Fig. 6. Squeeze cementing to plug off perforation of communication zones (Schlumberger, 1984)

3) Repair of casing leaks

Leaks may occur on the production well casing as a result of corrosion, splits, or joint failure. As a good objective to tackle

the case, cement is place in and around the hole in the casing and as a matter of fact, high pressure may extend the damage. As such, squeeze operation is normally performed at very low pressure.

4) Plugging of zones or perforations in multi-zone injection wells.

Diversion of injection fluid, water polymer solution, or gas is difficult to accomplish if no vertical permeability exist between zone and the isolation zone is satisfactory. The plugging of perforation in high permeability zone will direct the injected fluid to others (fig.7).



#### Fig. 107. Diversion of injection fluid (Schlumberger, 1984) 5) Plug and abandonment.

Squeeze to plug is also performed to block a depleted well or non-profitable producing well. This is performed at low pressure to avoid damaging of zone especially when there is tendency for economical exploitation in the near future.



#### Fig. 118. illustrations for plug squeeze job in a well (Schlumberger, 1984)

#### **Squeeze Cementing and Slurry Design**

The cement slurry (a suspension of solid) is exposing to a differential pressure against a filter of permeable rock regardless of the technique used for the squeezing job. This results in filtration phenomena, and the filtration cake deposited (in so many cases, on the fracture formation). The slurry loses part of its water to the permeable porous medium. Thus, the cake of partially dehydrated cement slurry is formed. Initially, the cake is formed as high permeability until the cement particle keep on accumulating (polymerize). The cake thickness and the hydraulic resistance increase (fig. 19). As a result, filtration of the porous medium decreases and the pressure require to hydrate it will increase (Marca, 1990). The filtration of the slurry and the rate of the filter cake up depend on:-

1)Formation permeability

2)Applied differential pressure 3)Time

4)Slurry capacity to loss fluid, when at down hole conditions.







Fig.20. Node build up using slurries of different water loss of 45 min squeeze (Marca, 1990)

The rate at which the slurry dehydration decreases is directly proportional to the fluid loss (fig. 20) when squeeze against permeable formation. Thus, when squeeze against low permeable formation, slurries with low fluid loss rate dehydrate slowly, as a result, the duration of the operation may be excessive. Slurries with high fluid loss rate dehydrate faster, as a result, the wellbore may become choked by the filter cake which otherwise would have accepted cement and bridged off (Marca, 1990). Therefore, the ideal squeeze slurry should be prepared to control the rate of cake growth and as well allow a uniform filter cake to build up over all permeable surfaces according to characteristics of the formation to be squeezed off.

#### **Zechstein Salt Formation**

Formation of zechstein evaporates are one of the biggest saline agent. The potential link between the marine residual brine has been over looked to be trapped from the halite of the oceans. The rapid growth of these halite crystals in NaCl saturated brine reported to have allowed the abundant trapping of fluid inclusion that preserves micro volume of fossils brine (kovalevich & Vovnyuk, 2010)

The analysis from the halite crystal usually gives the important information on the major chemistry of the formation water (Javier, et al., 2011).

#### **Chemical Evolution of Zechstein Brine**

The evolution of zechstein brine may have made a possible trend from the analysis of the primary inclusion fluid that may have trapped in a non crystallized halite crystal.

The fluid inclusion of zechstein brine below the anhydrite intercalation correspond to Na<sup>+</sup>, Mg<sup>2+,</sup> K<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> brine that are sulphate rich. All the range of its component is within the range of expected modern evaporated sea water during halite precipitations.

The variation of the chemical content may occur containing higher or less potassium and sulphate concentration between specific facies and thickness of the zechstein. As such, it cannot be attributed to normal daily brine evaporate of sea water.

Different brine type may also be recorded in a formation fluid inclusion composition with an evaporational trend to more concentrated brines. For example, sulphate rich brine may be found depleted in a specific face and later be found depleted in a subsequent zechstein face leading to brine with other ions. The sulphate ions may then inter return and observe in the next zechstein face, varying the fluid inclusion data's.

Calcium rich brine has been reported in halite intercalations in the basal anhydrite (Kovalevich, et al., 2008) but low density of sampling may prevent identification of the basin (chemical shift reported herein).

For better understanding of any work procedure, sample from each zechstein faces has to be analyst for its ion composition in order to have background and a well design structure for cement application in the formation.



Fig.24. Present day faces distribution map for Zechstein group Z2 (Javier, et al., 2011)

#### Cementing a Massive Salt Formation

It has been a long, the presence of salt dome and evaporate sequences in a formation been a problematic during drilling and completion jobs. Due to this zones high water solubility, it increases the difficulty in the successfulness of primary cementation. Thus, the slurry design can dissolve large amount of this material along with them. This result in modification of the cement slurry and consequently change the workability of the cement material.

Ludwig 1951 also reported the tendency of the salt zone to encroach the well casing before setting of the cement material (Erik B. Nelson, 1990). The non-uniformity of the formation also to sometime, exert a point loading on the casing string result in casing failure (Cheatham & McEver, 1964). The severity of this problem is routinely tackled with salt design cement but efficacy is still under controversy. In 1940s, salt cement was reported to have first used across salt dome in USA gulf coast which later became useful in area such as North Dakota and Montana as well as some certain area in North Sea.

The practice of these cement salt prevent the dissolution of the formation while the light salt concentration are antagonistic to the performance of the cementing additives such as dispersants and fluid loss additives which are formally design for fresh water system.

The light salt concentration of the environment tend to over retard the cement system and thus, the encroachment of the formation as well as the casing damage could occur even before the cement slurry set.

#### **Approaches Followed to Solve the Problems**

- Eliminating salt from the system
- Develop additive to have compatibility with the salt cement.
- Low displacement rate of salt free cement or very low concentration
- Used of semi saturated salt cement.

Low or salt free cement have been successfully applied in the Williston basin to prevent excessive dissolution of the formation.

In addition, due to the long time ionic disequilibrium cement work may ultimately fail. Therefore, the rate of ionic diffusion should be determine by the differences in the salt concentration between the cement and the formation (Erik B. Nelson, 1990), also shows that, fresh water contamination in cement slurry by a little of salt can alter the thickening time and also increase slurry viscosity and increase the fluid loss rate.

The use and design of salt cement is strongly depends upon the formation integrity to improve the placement characteristic of such cement additives such as hydroxycarboxylic acid is used as dispersants for the slurry. The use of fluid loss additives were also employed but problems of delayed compressive strength and over retardation is remained to be solved.

During the flows of this cement slurry, through the salt formation. A salt to slurry transfer physical phenomenon occur according to the Fick's law (Martins, et al, 2002) which is proportional to the concentration of the salt in the different formation to. The cement slurry can be salt saturated cement slurries.

• They have a good adherence in salt formation

• They have a good resistance to the environmental chemical attack

• The offer less dissolution of salt formation in the cement slurry

The use of low content salt cement slurries has the objectives to prevent any acceleration of cement set as a result of salt formation dissolving into the cement slurry (Van Kleef, 1989).

The most common slurries type that improve gel strength, and/or compressive strength are those that contain 3-5 % potassium chloride (KCl) used in place of NaCl (Sweatman, et al., 1999) and has been demonstrated to be used in gulf of Mexico.

The main salt of the oil basin are of the halite (NaCl), Carmnallite (KMgCl<sub>3</sub>.6H<sub>2</sub>O), Syvinite (KCl), Taquidrite (2MgCl<sub>2</sub>. 12H<sub>2</sub>O), and anhydrite (CaSO<sub>4</sub>) type, but no major effort has been employed yet on quantifying the mechanism of the salt transfer from the formation to the cement slurry.

Conclusion

The success as well as overcoming the problems encountered in sodium silicate treatment depends strongly on the placement operational design and how the operation is carried out considering from its preparation to its placement deep into the desire formation.

The sodium silicate squeeze cement used in wellbore flow treatment has proven successful in repairing of wellbore problems. Meanwhile, some silicate solutions depending on their mode of chemical preparation to penetrate very deeply into the formation thereby forming precipitate (gel like) compound to block the pores. However, the type and uniformity of this compound can be very greatly and as well as most important as whether the silicate solution can be beneficial to what degree. Some silicate absorbs internal moisture and begins to swell and produce internal pressure and stress and consequently damage the integrity of its job.

Sodium silicate gellation can successfully repair wellbore flow and penetrate deep into formation in area where even conventional cement alone fails. Sodium silicate is best practised when its mechanism of reaction with the cement is given priority and well known. Proper consideration should also be given to the concentration of the silicate in the system formulation as well as the particle distribution of the matrix. Chemistry of the surrounding environment should also be considered for excellent placement.

A well designed technique will be required to deliver the sodium silicate cement system to ensure is not diluted and dispersed by the flood environment. The silicate cement can be tailored to meet wide range of wellbore flow challenges by Modified ratio and pumping rate.

#### Acknowledgment:

The author of this article fully acknowledges the effort and contribution of Ian Pettit, Fluid Team Leader UIE, Shell, UK Limited, Altens Farm Road, Nigg Aberdeen Scotland United Kingdom.

#### References

Cheatham, J. B., & McEver, J. W. (1964). "Behavior of Casing Subjected to Salt Loading. *SPE*, paper SPE 828.yes

Debye, P. & Nauman, R.V. 1949, "The Scattering of Light by Sodium Silicate Solutions", *The Journal of chemical physics*, vol. 17, no. 7, pp. 664-664.

Eitel, W. 1964 "Silicate Science-Silicate Structure", Acdemic press New York and London, vol. 1

Erik B. and Nelson, P. D. (1990). 7 Special Cement Systems, In: Erik B. Nelson, Editor(s. *Developments in Petroleum Science*, 28, 7-1-7-14.

Greenberg, S.A. & Sinclair, D. 1955, "The Polymerization of Silicic Acid", *The Journal of physical chemistry*, vol. 59, no. 5, pp. 435-440.

Houlsby, A.C. 1990, "Construction and design of cement grouting" John Wiley & sons Inc. New York, pp. 65.

Houwink, R. & Salomon, G. 1965, "Adhesion and Adhesives" 2<sup>nd</sup> Edition, vol. 1, Elsevier Publishing Co. New York, pp. 434-438

Hurd, C.B. 1938; 1938, "Theories for the Mechanism of the Setting of Silicic Acid Gels.", *Chemical reviews*, vol. 22, no. 3, pp. 403-422.

Iler, R.K. 1953, "Polymerization of Polysilicic Acid Derived from 3.3 Ratio Sodium Silicate", *The Journal of physical chemistry*, vol. 57, no. 6, pp. 604-607.

Javier, G., Dion, I. C., Juan, J. P., & P., T. M. (2011). Zechstein saline brines in Poland, evidence of overturned anoxic ocean during the late Permian mass extiction event. *Chemical Geology*, 189-201.

Jurinak, J. J., Summers, L., & Bennet, K. (1989). Oilfield Application of Colloidal Silica Gel. *SPE International Syposium on Oil field chemistry*. houston, Texas: SPE.

kovalevich, V. M., & Vovnyuk, S. (2010). Fluid inclusions in halite from marine salt deposit: are they real microdroplet of ancient seawater? *geolocical Quarterly*, 401-410.

Kovalevich, V. M., Perty, T. M., N., S. S., Wieclaw, D., & Lytvyniuk, S. F. (2008). Geochemical aureoles around oil and gas accumulations in the Zechstein (Upper Parmian) of Poland: analysis of fluid inclusions in halite and bitumens in salt. *jounals of Petroleum Geology*, 245-262.

Krumrine, P. H., & Boyce, S. D. (1985). Profile Modification and Water Control With Silica Gel-Based Systems. *International Symposium on Oilfield and Geothermal Chemistry* (pp. SPE 13578-MS). Phoenix, AZ: SPE.

Lea, F.M. 1971, "The Chemistry of Cement and Concrete" 3<sup>rd</sup> Edition, chemical Publishing Co. Inc., pp. 179-249.

Liu, Y., Bai, B., & Shuler, P. (2006). Application and Development of Chemical-Based Conformance Control Treatments in China Oil Fileds, *SPE/DOE Symposium on Improved Oil Recovery* (p. SPE 99641). Tulsa, OK: SPE.

Marca, C. (1990). 13 Remedial Cementing, In: Erik B. Nelson, Editor(s), . *Developments in Petroleum Science*, 13-1-13-28.

Martins, A. L., Miranda, C. R., SPE, P., Santo, F. J., & Bove, A. (2002). Dynamic Simulation of Offshore salt Zone Cementing Operations. *IADC/SPE Drilling conference* (p. SPE 74500). Dallas, Texas: SPE.

Owusu, Y.A. 1982, "Physical-chemistry study of sodium silicate as a foundry sand binder", *Advances in Colloid and Interface Science*, vol. 18, no. 1–2, pp. 57-91.

Samari, E., Scott, D., & Dalrymple, D. (1998). Water Shutoff Treatments in Eastern Alberta: Doubling Oil Production, Decreasing Water Cut by 20%. *SPE/DOE Eleventh Annual Symposium on Improved Oil Recovery* (p. SP 39617). Tulsa OK: SPE. Schlumberger, L. (1984). *Cementing Technolgy*. London: Nova Communication Ltd.

Sugama, T. & Carciello, N. 1996, "Sodium metasilicatemodified lightweight high alumina cements for use as geothermal well-cementing materials", *Advanced Cement Based Materials*, vol. 3, no. 2, pp. 45-53.

Sweatman, R., Faul, R., & C., B. (1999). New solutions for subsalt well lost circulation and optimized primary cementing. *SPE annual technical conference and exhibition* (p. SPE 56499). Houston, Texas: SPE.

Van Kleef, R. .. (1989). Optimized slurry design for salt zone cimentations. *SPE/IACD Drilling conference* (p. SPE 18620). New Oreleans, Louisiana: SPE.

Yang, K., Song, J., Ashour, A.F. & Lee, E. 2008, "Properties of cementless mortars activated by sodium silicate", *Construction and Building Materials*, vol. 22, no. 9, pp. 1981-1989.