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

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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 MgCl2-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 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 gelation occurs to plug off these flow channels.

Sodium silicate chemistry
Sodium silicate (Na2O·SiO2) 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.

\[ \text{SiO}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{O} \cdot \text{SiO}_2 + \text{CO}_2 \]

Crushed or granular silica is crushed in an open furnace with soda at a temperature of about 1371°C (2500°F).

Sodium silicate is 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\(_2\) to Na\(_2\)O. E.g. A weight ratio of 3.22 parts SiO\(_2\) and 1 part Na\(_2\)O is referred to as 3.22 silicate ratio (i.e. SiO\(_2\):Na\(_2\)O = 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 its viscosity rises due to neutralization of the SiO\(_2\)-Na\(_2\)O bond, or overcomes by chemical reactions; the two components became independent of each other.

When SiO\(_2\) tend to precipitate by polymerization in form of silicic acid (H\(_2\)SiO\(_4\)) high percentage of Na2O remains in the solution forming NaOH. Therefore, in sodium silicate solution, the positive Na\(^+\) cation and the negative SiO\(_2\)\(^2-\) 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\(_4\)), bonding together by complex polymerization into chain network.

![Fig. 1. Silicate tetrahedral structure](image)

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).

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\(_3\)SiO\(_4\)) or metasilicic acid (H\(_4\)Si\(_2\)O\(_7\)), 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\(_2\):Na\(_2\)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 \(\text{Si}+\) 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](image)

![Fig. 4. combination of a mono and dimmer silicic acid to produce trimer](image)

Once the OH group are replace by O\(^-\) ion with higher polarizability, it condense with final generesis to a silica hydrogel shorten the Si\(^+\)– Si\(^+\) 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:

\[
\text{Silicate} + \text{Water} \rightarrow \text{Silicic Acid} + \text{Gel}
\]

**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\(_2\)/Na\(_2\)O ratio: Polymerization is obtained faster with higher ratio of SiO\(_2\)/Na\(_2\)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\(^-\) and F\(^-\) delayed the gelation process, participating in the solubility of silica. If F\(^-\) is present; it can undergo true chemical reaction and form (SiF\(_6\))\(^2-\) 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\(_2\)(H\(_2\)SiO\(_4\)) . 8H\(_2\)O. Dissociated as follow:-

\[
\text{Na}_2(\text{H}_2\text{SiO}_4) + 8\text{H}_2\text{O} \rightarrow 2\text{Na}^+ + \text{H}_2\text{SiO}_4^2- + 4\text{H}_2\text{O}
\]

Greenberg and Sinclair, 1955 report that, the silicic acid H\(_3\)SiO\(_4\) have low ionization constant (K\(_1\) = 1x10-9.8, K\(_2\) = 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 CO\(_2\), 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\(_2\)**

CO\(_2\) gas can react with Na\(_2\)O.SiO\(_2\) to produce mono-silicic acid decreasing the pH of the region and enhancing gel formations

\[
\text{Na}_2\text{O.2SiO}_2 + \text{CO}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{Si(OH)}_3 + \text{Na}_2\text{CO}_3
\]

Ionically;

\[
\text{Na}_2\text{O.2SiO}_2 + 5\text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 2\text{Si(OH)}_3 + 2(\text{OH})^- + \text{CO}_2 + 2\text{H}^+ + \text{CO}_3^{2-} \quad \text{(carbonic acid)}
\]

OH\(^-\) and H\(^+\) combine to give water reducing the pH of Na\(_2\)O.2SiO\(_2\) solution.

\[
\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}
\]

Importantly;

\[
\text{Na}_2\text{O.2SiO}_2 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + (\text{SiO}_2.\text{H}_2\text{O})
\]

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

The Na\(^+\) 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:-

\[
\text{Na}_2\text{O.}\text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{Dehydration} \rightarrow \text{SiO}_2\text{H}_3 \quad \text{(Glassy-H}_2\text{O)}
\]

**Sodium silicate dehydrations and CO\(_2\) reactions**

**Fig. 7. Reaction of sodium silicate solution with CO\(_2\)**

**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.
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 minutes (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 produced 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 Na₂O to the source material ratio by weight. Thus, Na₂O 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.

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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⁺ ion in the cement solution make it more viscous by ion exchange reaction between the Na⁺ of the sodium silicate and the Ca²⁺ 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 (Na₂SiO₃) mixed with the cement as the principal ingredient; Ca(OH)₂ combine with the silicate ion (SiO₄³⁻). Silicate-cement gel is formed. The formation mechanism can be illustrated as follow:

\[
\text{Na}_2\text{SiO}_3 + \text{Ca(OH)}_2 \rightarrow \text{CaSiO}_3 + \text{Na}_2\text{OH} \\
\text{Na}_2\text{SiO}_4 + \text{Ca(OH)}_2 \rightarrow \text{CaSO}_4 + \text{2NaOH}
\]

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).

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 Ca²⁺ 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 Ca²⁺ and Mg²⁺. 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.
As C₃A also one of the principal component of the cement, due to that the cement suspension tend to produce CA or CA₂ which react with Na₂SiO₃ and led to the formation of sodium calcium silicate hydrate

\[
\text{CaO}_3\text{Al}_2\text{O}_5 + 3\text{Na}_2\text{O}_3\text{SiO}_2 \rightarrow \text{[Na}_4\text{Ca}_2\text{Si}_2\text{O}_9\cdot\text{H}_2\text{O]}
\]

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 [\(3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2\)] present in the cement solution to yield a dense product which is an intermediate that enhance the degree of crosslinking between the cement matrix and also improve the cement interfacial bond (Sugama, Carciello 1996).

\[
[\text{3Al}_2\text{O}_3\cdot2\text{SiO}_2] + \text{Na}_2\text{SiO}_3 \rightarrow [\text{NaAlSi}_2\text{O}_6\cdot\text{H}_2\text{O}]
\]

**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](image)

**Squeeze cementing**

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 (Marcia, 1990). The cement solids developed a filter cake on the fracture face and/or bridge the fracture (Marcia, 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:-

1) **Repairing of primary cementing jobs.**

Primary cementing jobs may fail due to cement by passing the mud (channeling) 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)

![Fig. 85. Perforations between top and bottom intervals](Schlumberger, 1984)

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.**

Division 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. 129. Cake permeability and dehydration rate as a function of fluid loss additives (Marca, 1990)

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 observed 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⁺, Mg²⁺, K⁺, Cl⁻, SO₄²⁻ 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 determined 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.

The cement slurry can be salt saturated cement slurries. 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 (Martin, 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 (KCI) 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 (K(MgCl,6H2O), Syvinite (KCI), Taquidrite (2MgCl2, 12H2O), and anhydrite (CaSO4) 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 flow environment. The silicate cement can be tailored to meet wide range of wellbore flow challenges by Modified ratio and pumping rate.

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