A fit for purpose expandable sealant for demanding conformance applications

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Abstract

Natural and induced fractures between injection and producing wells are a common and challenging problem that reduces the economic feasibility and life of a well. Traditional treatment solutions have typically relied on cement, resins, polymers or simply drilling a new well. A low cost, expandable silicate-based sealant has been developed and successfully field trialed as an alternative technology. Two features have been added to conventional silicate-based sealants to make this system more amendable to a wider range of conformance applications including fracture sealing. The previously mentioned expansion characteristic is achieved by the use of formulated metal slurries to allow for a variable expansion rate. The controlled generation of a foam material serves to decrease viscosity to allow for better control of placement within the fracture. The expansion mechanism allows the treatment to remain under pressure while setting, augmenting efficacy in placement. Once expanded; a closed cell foam is created that provides a tight, form fitting seal. The other feature in the sealant is the incorporation of recent advances in geopolymer chemistry that results in a higher strength and more durable plug. The paper will review the chemistry and basic formulations and present case histories on the product.

Introduction

Many downhole repairs require a material that will fill and tightly seal a fracture or void space. The “tightly seal” component can be particularly challenging and is often missing from most chemicals and cement systems. Although the mechanisms vary, most material lose some volume upon setting. The loss of volume can be further accentuated by the influx of liquids as well as changes in pressure and temperature. This can lead to the sealant being extruded or pushed/flushed away from the treated zone. Ultimately the overall loss in volume and/or displacement of plugging products can result in poor bonding between the sealant and surface of rock and/or casing. This problem is often encountered in trying to seal natural or induced fractures between injector and producer wells and is particularly challenging when CO2 is used for enhanced oil recovery.

Recognizing the need for additional treatment options, a collaborative effort took place between chemical manufacturer, service company and operator to develop a fit for purpose expandable sealant based on sodium silicate chemistry.

As background to the development effort, sodium silicate treatments have been used for close to 100 years. Over this time, there was a lull in popularity as polymers and resins were promoted as an easier to use technology that could be remediated if incorrectly placed in the reservoir. Over the last few years, there has been resurgence in using sodium silicate for cement remediation as well as conformance applications. The swing back towards silicate-based systems is being driven by their excellent HS&E properties, durability and cost effectiveness. Risks associated with improper placement in the reservoir have been mitigated by better modeling of gelation kinetics and improvement in diagnostic and placement techniques.

Sodium silicate sealants can be run with or without solids material contained within the sealant. A solids free material system is typically based on sodium silicate, water, and a setting agent. As a low viscosity solution, it can be placed deep into a reservoir for water blockage or profile modification. Microfractures can be filled their entire length that would otherwise quickly bridge-off using microfine cement or solids containing sealant.

The addition of solids material to a silicate solution is multifunctional and can offer several performance enhancements. The solids can act as a bridging material, improve strength and durability, aid in controlling density and reduce overall costs. Typically, the selection of filler/bridging is based on a solid that is low cost, easily sourced and has minimal to slight reactivity towards the silicate. Under this umbrella would fall solids such as; barite, calcium carbonate, clay, hollow glass spheres, silica flour, walnut hulls, etc. The use of relatively inert material has the advantage of simplifying the chemistry while still producing an effective sealant.

but the resulting product can offer several performance enhancements over Portland cement or other sealants. Development efforts within oilfield industry has focused on developing, modeling and testing geopolymers for plug and abandonment as well as lost circulation control. These particular applications benefit from the performance properties commonly associated with geopolymers; high compressive strength, tolerance to contamination by oil-based muds, chemical durability self-healing characteristics, good pumpability and excellent environmental credentials. Aspects
of geopolymcer technology were incorporated in the development of an expandable silicate sealant. The developed formulations could be considered geopolymcer “ish”. The resulting material would have some polymeric linkages of Si-O-Al but less than would be found in a true geopolymcer. These formulations also differ in they still use a setting agent for the alkali silicate. The use of a setting agent allows for quicker and predictable set times at a given temperature.

Chemistry

Sodium silicate chemistry is condensed into a couple of paragraphs to provide a basic overview and the foundation for the development of an expandable silicate system. There are several excellent papers that provide further details on silicate chemistry as it pertains to conformance applications.\textsuperscript{8,9}

The manufacturing of sodium silicate provides a starting point to understanding the chemistry and the influence on final alkalinity. Sodium silicate is produced in a furnace by fusing high purity sand with soda ash. Sufficient sodium is fused onto the silica to allow the resulting glass to be dissolved by high pressure steam forming an aqueous solution of sodium silicate. The ratio of sand and soda ash is controlled so as to produce sodium silicates with different weight ratios of SiO$_2$: Na$_2$O. A 3.2 ratio sodium silicate can be thought of as having 3.2 kilograms of sand for every 1 kg of alkali.

$$\text{Na}_2\text{O} + \text{SiO}_2 \rightarrow (\text{SiO}_2)_{1-x}(\text{Na}_2\text{O}) + \text{CO}_2 \quad x = 1.6 \text{ to } 3.2$$

Almost all chemical, physical and performance properties of sodium silicate are determined by the ratio of SiO$_2$:Na$_2$O. The practical range of ratios produced in a furnace is 1.6 to 3.2. Conformance applications have predominantly selected 3.2 (lowest alkaline, most silicious form) as the preferred ratio of sodium silicate. Compared to lower ratio sodium silicates, a 3.2 ratio sodium silicate system is easier to polymerize and set. Upon polymerization, silica gels derived from ~3.2 ratio sodium silicate tend to provide higher compressive strengths, better durability and is less prone to shrinkage vs. gels made with lower ratio silicates.

For geopolymcer formulations, the preference is usually towards low ratio silicates. The higher alkalinity being necessary to dissolve and activate aluminum oxide and silica. As will be presented later in the paper, the higher alkalinity can be desirable in formulating an expandable silicate-based with quicker and more dramatic gas generation.

The other form of sodium silicate selected for this development effort was Aqueous Alkali Alumino Silicate (AAAS). This is a non-conventional form of sodium silicate and is based on a pre-primed silicate that includes aluminum dissolved into the silicate. It is a clear soluble liquid silicate that is stable and visually no different than other forms of liquid sodium silicate. The chemistry of this product is unique and has been detailed by Miller\textsuperscript{10} where it was investigated as a lost circulation material in drilling fluids. As with conventional sodium silicate, the AAAS can be triggered to polymerize via a reduction in pH or precipitated via the reaction with multivalent metals. Compared to conventional sodium silicate, the AAAS material was shown to have a high tolerance to oil and salt contamination. In contrast to a 3.2 ratio sodium silicate, the AAAS has an associated aluminum and significantly more alkalinity. As will be presented, control of type and form of alkalinity is a key feature for the expandable silicate system.

<table>
<thead>
<tr>
<th>Material</th>
<th>densit \textsuperscript{(g/cm$^3$)}</th>
<th>size (micron)</th>
<th>SiO2 (%)</th>
<th>Na2O (%)</th>
<th>CaO (%)</th>
<th>Al2O3 (%)</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass Fill\textsuperscript{®}</td>
<td>2.5</td>
<td>~45</td>
<td>-74</td>
<td>13</td>
<td>10.5</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Adversa\textsuperscript{®} Zeolite A</td>
<td>2.4</td>
<td>~5</td>
<td>33</td>
<td>17</td>
<td>0</td>
<td>28</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 1. Properties of Sodium Silicate Solution

Table 2: Physical and chemical properties of filler material

![Figure 1a: Zeolite A](image1)  ![Figure 1b: Glass Fill](image2)

Hydrogen Generation in an Alkali Environment

The in-situ generation of hydrogen in Portland cement served as a starting point for understanding the chemistry, application and limitations. Metals that are thermodynamically favorable for the generation of hydrogen include; aluminum, iron, magnesium, lithium, sodium, potassium, rubidium, cesium, calcium, barium, strontium, radium and zinc powders. From
this list, aluminum and zinc were selected as the most suitable metals. While gas generation is thermodynamically favorable, the protective oxide film on the aluminum and zinc surface prevents corrosion and generation of hydrogen. To initiate the hydrogenating reaction, the oxide must be removed by using a source of alkaline such as NaOH or in the case of a cement slurry, Ca(OH)$_2$.

\[
\begin{align*}
2\text{Al}(\text{s}) + 2\text{OH}^- (\text{aq}) + 6\text{H}_2\text{O} &\rightarrow 2\text{Al}(\text{OH})_4(\text{aq}) + 3\text{H}_2\text{O} \\
\text{Zn}(\text{s}) + 2\text{OH}^- (\text{aq}) + 2\text{H}_2\text{O} &\rightarrow \text{Zn}(\text{OH})_2(\text{aq}) + \text{H}_2\text{O}
\end{align*}
\]

For Portland cement, once it mixes with water it hydrates to form calcium-silicate-hydrate (CSH) as well as Ca(OH)$_2$. The Ca(OH)$_2$ saturates the aqueous phase raising the pH to ~12.7. While there is variation in types of Portland cement and water to cement ratio, the type and amount of alkalinity is more or less fixed and thus is not an option for control of gas generation rate.

In contrast, sodium silicate-based system has a wide range of alkalinity with a pH range of ~11 to 13.1. The pH/alkalinity being controlled by the ratio of SiO$_2$:Na$_2$O. (i.e. 1:6 to 3:2:1). Per figure 1, there is also control over the type of silicate ions in solutions. For the low ratio sodium silicates, the dominant form is H$_2$SiO$_4^{2-}$ as silicate ratio increases there is a transition to H$_3$SiO$_4$ as well as H$_4$SiO$_4$. The H$_2$SiO$_4^{2-}$ being more aggressive at removing oxide films. The control over the type and amount of alkalinity allows for much more control of the gas generation rate and allows for much longer expansion rates.

Some control of gas generation rate can be achieved by manipulation of the properties of the aluminum powder. These include:
- surface area of the metal powder
- coated vs. uncoated metal
- in the case of slurried material, the choice of carrier fluid

The other lever for control of gas generation is the choice of metal. Portland cement relies on aluminum as the metal of choice. The use of zinc retards the hydration reaction and decreases the mechanical properties of the Portland cement (reference). In contrast, an alkali silicate-based system is amendable to the use of both aluminum and zinc.

**From Lab to Field**

The early adopter for the first field trials was an operator that had past success with using sodium silicate for conventional conformance treatments such as blocking high permeability zones in the reservoir. The development of a system that could expand and tightly seal offered promise for the more common and challenging problem of natural and induced fractures between injector and producer. An expandable silicate-based sealant had the potential to provide a cost effective solution. A collaborative effort began with the pumping company and chemical manufacturers to develop a fit for purpose sealant.

Outlined by the operator as the starting point:
- setting and expansion time of ~4 hrs. (to allow adequate placement in the fracture)
- reservoir temperature of ~55°C
- starting density of ~1.5
- capable of withholding 22 MPa of pressure
- bridging size of ~5 micron (similar to microfine cement)
- cost effective

Given the downhole temperature and pump time, zinc was selected over aluminum to allow for a slower rate of gas generation. Initial formulation work was done at temperature and ambient pressure. Once the formulation was finalized, it was tested using a consistometer. Table 3 presents the formulation that was developed for trial. The silicate was a 3.2 ratio sodium silicate and the filler was a 5 micron alumino silicate powder. Figure 3 shows an optical micrograph. The expansion rate was calculated to be ~15%.

<table>
<thead>
<tr>
<th>Silicate</th>
<th>Set. Agent</th>
<th>Zeolite A</th>
<th>Expand Agent</th>
<th>Final Density</th>
<th>Comp. Strength</th>
</tr>
</thead>
</table>

![Figure 2: Distribution of silicate species at 25°C as a function of pH](image.png)
Table 3: Properties of Sodium Silicate Solution

<p>| | | | | | |</p>
<table>
<thead>
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</thead>
<tbody>
<tr>
<td>75</td>
<td>6</td>
<td>25</td>
<td>1</td>
<td>1.3</td>
<td>~1000psi</td>
</tr>
</tbody>
</table>

The bottom line is 1 mm long. Picture was taken on a Leitz microscope with Ultrapak optics at 1.68x.

Concurrent with developing a fit for purpose expandable sealant, the operator identified a candidate well for the first field trial. Identified as a key criteria for success was the running of diagnostics to properly understand the nature of the problem. The diagnostics also served to determine the applicable placement technique. Learnings from past conformance attempts were studied to understand what went right and what led to deficiencies.

**Case Histories**

The first trial involved an injection well that had CO\textsubscript{2} communicating almost immediately with producer, resulting in high gas production with little oil benefit. Spinner logs showed >80% of the CO\textsubscript{2} entering bottom perfs. This was not surprising as this layer of the reservoir is known to be prone to natural fractures. Transit time of dye tracer suggested the reservoir flow path was small and in the range of ~2 m\textsuperscript{3}. Past attempts to shut down fracture paths through the bottom set of perfs have proved short lived. The durability associated with a silica-based and newly developed expansive characteristics of the silica sealant held promise to address previous shortcomings. The chemical resistance and expansive properties meant that extra care was required to ensure that it did not enter the production well. Once placed, the chemical options for restoring injectivity are basically limited to the use of hydrofluoric acid.

Leading up to the trial an additional tracer test was run. This allowed for slight modifications to the program ahead of the trial. The gathered information allowed the developed formulation to be tuned prior to being at the job site. Minor adjustments were made to the volume requirements for fresh water, overall volume of mixed product, set times, viscosity and provided confirmation of downhole temperature.

Given the fracture was at the bottom perforation it was not isolated with a packer. Placement would be rigless and pumping was down the tubing. The expandable silica-based sealant was prepared using cement pumping unit. Care was taken to wash tank and lines so there was no potential cross contamination. Given the small volume of the first trial, the treatments were prepared using 50 lb bags of dry material with the liquid silicate being in totes. Just prior to the trial date, a cold front entered the area and did require additional planning and the use of a heated van to allow for working in -28°C weather. Figure 4a, 4b provide an overview of the set-up. Material was prepared and pumped with a plan to stop after pumping the pill volume or upon hitting the max injection pressure (24 MPa bottom hole). Pressure began to build at the end of the pump cycle but stayed low enough allowing a water-based sweep to be pumped ensuring no sealant was in the tubing.

Post treatment; the oil production remained the same but gas production dropped 80% by having the natural fractures filled with the expanding sealant. A follow up spinner log was conducted and it appears that with the main fractures filled other natural fractures in the same lower set of perfs were now taking the majority of the gas injection. This suggested that only the fractures directly connected to the producer were blocked. A learning point was that a larger treatment volume might have filled additional fracture pathways.
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2nd case history

The 2nd case history involved an overall complex operation where a previous successful producing well had turned to producing ~400m³ per day of 100% water. The decision was made to run a 4.5” liner and stage tool into the well. The overall plan was to perform a 2 day pumping job:
- Day 1: Pump the expanding silicate
- Day 2: Pump a cement slurry to circulate cement behind the liner

The stage tool would be opened to leave the liner open in order to obtain a federate. Then, close casing and pump the expanding silicate down tubing and through the stage tool with liner hanger open. It was expected that the majority of the silicate would enter the fracture with casing closed. The next step would be to over-displace the silicate with water by calculating the volume behind the 4.5” liner using the log info. The silicate would then be left overnight to set and in the morning a feedrate performed in preparation to pump the second stage of the job utilizing a cement slurry. A dart would be dropped to close the stage tool and set the liner hanger.

A quick recap of each day is important to review as some plans changed based on feed rates and pressures seen.

Day 1:
Pumping lines were filled with water and pre-set planned volumes (stages) of water were pumped. At each stage, rate was controlled, and pressures were monitored. This process continued until stage tool setting pressure was reached and stage tool was opened. Once the tool opened, the casing was rotated to come off the liner.

The sodium silicate system was mixed and all 10m³ were pumped followed by a specially designed spacer and then water to fully displace the silicate system into the formation.

Day 2:

After all the tubing was pulled form the well, it was time to pump the second stage of the job which was the cement slurry. The water preflush was pumped to establish a federate but pressure was seen. Small volumes of water were pumped in stages and pressures continuously rose to >5 MPa and it was decided to pump down the casing. A federate was established at 300l/min and 6.2 MPa so it was decided to reduce the cement volume by 50% for not knowing exactly where the restriction was in the wellbore and could not risk not getting the stage tool closed. The cement slurry was batched up and all 3m³ were pumped and displaced until the liner tool pressured up. The rig then spun off the liner and 37m³ of water was pumped to flush the drill pipe.

The following days and months have shown some interesting and promising results. A bond log was run on the liner and it was found that a small percentage of the liner had enough cement and a good bond. It was also clearly identified that the stage tool had cement around it with a good bond. Ultimately it was determined that the original volume of cement should have been pumped but there was a bridge somewhere that prevented full circulation. This situation created a chance that pumping the original volume of cement may have prevented the operator from getting the stage tool closed – this was not an option.

Ultimately although cement placement and isolation didn’t exactly match what was set out to accomplish, the success was seen in the results from the 2-day pumping operation. Before the job, the well was on vacuum. As mentioned previously, on day 2, the pressures seen before pumping the cement slurry were 6MPa down the tubing and pressured up to 4 MPa when pumped down the casing. It was evident the silicate had set and blocked something off. This was with the liner top packer open and stage tool open so we would have been attempting to feed the fracture. The well was acting completely different after the silicate job.

A few days after the completion of Day 2, the decision was made to go ahead and drill out the stage tool and place the well on production. The operator would then see if the expanding silicate, liner, two inflate packers and the good sections of bonded cement was enough to hold back the fracture. Ultimately, if it didn’t hold back the fracture, remedial cementing would have to be performed.

Post treatment results have been very favourable. A couple weeks after putting the well back on production showed that this particular well moved from 400 m³/day total fluid at 100% water to 81 m³/day of total fluid at 88% water cut. At the time of writing this paper (7 months from treatment), the well is still performing at 80 m³/day of total fluid and 90% water cut. Overall, the operator is pleased in seeing continued performance and quick ROI for this expanding silicate.
treatment.

Conclusion

Recognizing that industry is looking for a broader range of options, research was launched to develop compressible silica-based sealant using gas generation additives. Lab results indicate that gas generation rate can be controlled from seconds to days. Compressive strength is proportional to expansion as well as choice of solids material. The selection of material with moderate reactivity seems to strike a good balance at producing a material that could be easily formulated and produced a final product with the desired strength and durability.

Moving from lab to field, a collaborative approach was taken to ensure material could be pumped and meet the requirements of the candidate wells. The last trial was particularly encouraging with increased oil production and decreased water production. Additional trial work is planned to further validate the technology.

Acknowledgments

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