

## Mitigating interfacial debonding by use of an expandable silicate-based plug

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### Abstract

Gas and fluid migration as the result of poor zonal isolation is a common and universal problem. Beyond decreased economic performance, there is increasing regulatory pressure to block the out of zone flow of gas and liquids. One of the more common pathways to higher zones or surface is along the cement interfaces. The causes for interfacial pathways have been well covered in the literature and include; poor wellbore preparation prior to cementing, the loss of hydrostatic pressure as cement transitions to a solid and downhole changes in pressure and temperature.

The use of gas generating additives in cement has a long history of use for improving annular sealing. In particular, the addition of aluminum powder to Portland cement for the in-situ generation of hydrogen. Sodium silicate shares with Portland cement the necessary alkali environment for a similar generation of hydrogen. However, different setting mechanisms along with a lower and broader range of alkalinity provide conditions to formulate a diverse range of expandable sealing materials. Control of expansion and set times are further extended by the development of zinc and aluminum slurries specific for use in an alkali silicate environment. The use of environmentally friendly carrier fluid also addresses handling concerns associated with powdered metals.

This paper discusses the chemistry and physical properties of an expandable silicate-based grout. The focus will be application of this material for wellbore repair but will also cover the use in other applications such as a lost circulation material, diverting pill as well as plug & abandonment.

### Introduction

The use of sodium silicate for cement remediation as well as lost circulation is well established if somewhat overlooked technology<sup>1</sup>. Over the last 5+ years, there has been a resurgence in using sodium silicate for cement remediation as well as conformance applications<sup>2</sup>. This has been driven by

a need for a solids free product that is cost effective as well as environmentally friendly. The HS&E characteristics being critical for remediating treatments taking place above the base of ground water.

Aqueous sodium silicate is set by inducing a precipitation and/or polymerization reaction. In the precipitation reaction, the sodium silicate reacts with a multi-valent cation to form a metal silicate. The classic formulation is a CaCl<sub>2</sub> solution followed by a spacer followed by sodium silicate. When the sodium silicate comes into contact with Ca<sup>2+</sup> it quickly reacts to form calcium silicate. The polymerization reaction is a little more complex. It involves inducing a drop in pH in a silicate solution causing the silicate molecules to polymerize into a silica gel. Compared to the precipitation reaction the set times can range from several seconds to several days.

In cases where silicate is set by the polymerization reaction the formed silica gel can show signs of;

- syneresis (i.e. prone to shrinking)
- brittleness

The issue of shrinking/contraction is not unique to sodium silicate and is known to occur in resin, polymers as well as Portland cement. The problems associated with cement contraction have been known for decades and it has been an on-going field of research. Degree of contraction is driven by chemistry as well as factors such as loss of water, thermal changes and pressure differentials. In the case of cement, several methods have been proposed to counteract the cement shrinkage in oil field applications<sup>3</sup>. Somewhat surprising was there has been little effort to develop expandable, silicate-based plugs.

The use of aluminum as a gas generating additive was proposed for structural concrete and later applied to oil well cement<sup>3</sup>. When aluminum or other suitable metal is added to the cement slurry, the high pH environment results in the production of minute hydrogen gas bubbles. The alkaline

environment of sodium silicate suggested that a similar approach could be adopted to improve the sealing capability of silicate-based plugs.

As Portland cement hydrates, the typical pH of the pore solution is ~13 compared to a pH range of 11 to 13.1 for aqueous sodium silicate. The pH of sodium silicate is controlled through by the ratio of SiO<sub>2</sub>:Na<sub>2</sub>O. (i.e. 1:1 to 3.2:1). Alkalinity is controlled via the concentration of sodium silicate in solution. Given the latitude for controlling both alkalinity and pH, it became evident that a much broader range of expansion rates were possible vs. Portland Cement.

The idea of expansive silicate-based plugs represented a new area. Prior to devoting resources and setting R&D direction, operators and service companies were consulted to better understand desired performance properties. This also allowed for determination of initial target applications. As was anticipated, remedial cementing represented an immediate opportunity. Lost circulation was the second most cited application. The response for desired performance properties was less narrow and resulted in a broad range of characteristics;

Slurry density – 1.0 to 2.0 g/cm<sup>3</sup>

Operation Temperature – 20C to 250C

Set & Expansion Times – 10 minutes to days

### Silicate Selection & Formulation

Initial development work began with existing, commonly used silicate-based plugs, the objective being to improve these formulations by adding the property of expansion. This helped narrow the range of starting materials. The preferred sodium silicate was a 3.2 ratio (see table 1). This is the highest ratio, least alkaline form of sodium silicate that is made by furnace technology. It is the most widely used product for cement remediation as well as conformance applications. The lower alkalinity was deemed desirable since it would allow for longer expansion times than would be possible with Portland cement.

While the goal was to formulate with proven, commonly used materials, a deviation was made in the second choice of sodium silicate. A recently developed product is an aluminum modified sodium silicate. The product is described as an aqueous alkali alumino silicate or “AAAS”<sup>4</sup>. The appeal of the AAAS product was its tolerance to oil and oil mud contamination vs. conventional silicates. As lost circulation and remedial cementing were the focus applications, it was important the base product could be robust to cases of oil contamination.

Table 1: Properties of Sodium Silicate Solution

	Na2O (%)	SiO2 (%)	Al2O3 (%)	Na2O: SiO2	Solids (%)	Density
“AAAS”	16.2	27.9	1.6	1.7	45.7	1.6
3.2 ratio	8.9	28.7	-	3.2	37.6	1.38

The other materials used in formulating a silicate-based plug are; setting agent, filler/bridging material and water. Of the extensive list of setting agents<sup>5</sup>, there are a dozen or so that would be considered common place. These included; citric acid, sodium acid pyrophosphate, urea, lactose, propylene carbonate and triacetin. As will be presented later, the metal slurries were formulated so as to incorporate the setting agent.

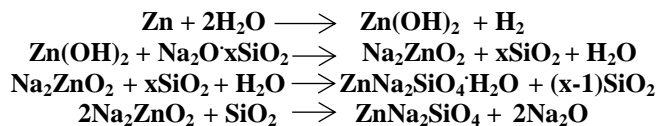
The biggest variable in formulating silicate based plugs proved to be choice of filler/bridging material. Control of initial density was primarily achieved by choice of filler/bridging material. In order to achieve the wide range of starting densities, filler material had specific gravities ranging from 0.4 to 4.2. This included; hollow glass spheres, walnut hulls, zeolite, calcium carbonate, fly ash and barite. Of the listed bridging material, some material would be considered reactive towards sodium silicate and others inert.

### Metal Selection/Expansion Rates

Similar to Portland Cement, expansion rates can be regulated by several factors to allow for desired reaction times under downhole applications. Similar to expandable cements, it is optimal to have the generation take place between the time of placement in the subterranean open space and the early setting stages of the soluble alkali silicate. The gas generation rate can be controlled by several factors;

- type of metal powder
- surface area of the metal powder
- coated vs. uncoated metal
- in the case of slurried material, the choice of carrier fluid
- temperature
- grade of soluble alkali silicate

Aluminum is the metal of choice for the in-situ generation of gas in Portland Cement. Aluminum represented a good starting point for sodium silicate-based systems as did zinc. In the case of zinc, it allowed for a slower expansion rates and assisted in setting the silicate. As well as insolubilizing the silicate, zinc has the ability to help insolubilize sodium. (per formula 1).



The durability / insolubility of zinc silicate is supported by zinc rich, silicate coatings which are used in a number of severe environmental conditions where HPHT resistance is required.

Aluminum has the advantage of a quicker reaction for use in a two part system and can be used closer to water tables. The aluminum and zinc are available in flake, granular, coated, uncoated, and in slurry form. The form of choice for the work done was the metal particles suspended in a slurry. The use of slurry mitigates handling issues associated with powdered metals. These issues include EH&S concerns with the reactivity of the metal, preventing the metal from reacting with ambient conditions outside the target area. Additionally, the slurries were formulated to be pourable liquids. This allows for easier handling on site with standard pumping equipment. The carrier fluid in the slurries can function as a setting agent for the alkali silicate. Examples of suitable carrier fluids that can suspend and carry metal while acting to set sodium silicate include, but are not limited to, acid generating liquids such as propylene carbonate. The carrier fluid can also serve to retard the expansion reaction via the use of organic carrier fluids, such as mineral oil, polyalphaolefins, polyethylene glycol, or propylene glycol. The 4 slurries which were designed for this application all have a 52% metal content. Two of the slurries are aluminum based and two of the slurries are zinc based. The two different carrier fluids were chosen based on EH&S characteristics, economics, and reactivity with silicate. The two carrier fluids chosen as noted above are propylene carbonate which will react and set silicate and polyethylene glycol which will not react with silicate, but will give the added benefit of being a freeze point depressant. Both have excellent EH&S ratings and are readily available. All 4 slurries are thin, pourable liquids for ease of use.

### Expansion Rate & Properties

Presented is a cross section of formulation work to measure expansion rates and properties. Degree of expansion was typically measured as a function of the change in volume and density. Volume expansions of four times original were easily produced under ambient and mild pressure. In-house testing was limited to a pressure vessel with a rating of 110 psi and 120C. Earlier work indicated that increasing pressure produced a moderate decrease in expansion but samples still exhibited expansion under pressure<sup>3</sup>. It was assumed the same trend would be seen with a silicate-based plug. Future lab

work will include the use of consistometer to better simulate downhole pressures.

This paper focuses on the expansion properties of a silicate-based plug. Other properties measured included;

- control of workability and set times
- compressive strengths
- HS&E characteristics
- Cost

As comparison to original work with aluminum powder, a simple 1:1 weight to weight mixture was made with Class F fly ash and sodium silicate (AAAS) was measured against the reported linear expansion of API Class A Cement<sup>3</sup>. Similar to original experiments, expansion took place at 80F.

Table 2: % Expansion API Class A Cement vs. Silicate

% Aluminum powder	API class A 0 psi	API class A 3000 psi	AAAS:Class F Fly Ash 0 psi
0.0	-	-	-
0.05	11.8%	0.71%	213%
0.1	17.9%	0.92%	233%
0.25	24.0%	1.64%	280%
0.5	56.5%	2.64%	317%
1.0	57.2%	5.17%	350%

All formulations showed >200% of the expansion rate taking place in the first 30 minutes. Testing took place upon achieving initial expansion or at 24hrs. Table 3 shows that expansion can continue to at least 7 days. Of note is the compressive strength showed a dramatic increase over 7 days. The increase in compressive strength was attributed to the reaction of zinc with silicate. The compressive strength of the expanded plugs were significantly lower in strength vs. the non-expanded controls. This was largely attributed to the differences in density.

Table 3: Compressive strength vs density

	24 hr @ 50 C		7 days @ 50C	
	Density	Comp. strength	Density	Comp. strength
No Zinc	1.87	1130 psi	1.85	1582 psi
2.3% Zinc	0.58	135 psi	0.50	605 psi

For sealing microchannels, it is often desirable to use a solids free material to ensure depth of penetration and avoid bridging at fracture openings. Zinc flake was investigated in a 3.2 ratio sodium silicate solution using lactose as a setting agent. While this is not quite solids free, the zinc represented 2.5% by weight of sodium silicate treatment. This would be in comparison to ~60% solids in a cement slurry.

Table 4: expansion & compressive strength without bridging material

	Initial Density g/cm <sup>3</sup>	Final Density g/cm <sup>3</sup>	Comp. Strength psi
No Zinc	~1.46	1.4	12
2.5% Zn	~1.46	0.81	39

Compressive strength was noticeably decreased by removing bridging material (table 4). Similar to the previous example the increase in strength was attributed to the reaction of sodium silicate with zinc.

In the case of sealing microchannels, a case can be made that strength is less important vs. a tight durable seal that is resistant to extrusion. Past research has indicated that a silica gel can resist extrusion pressures of 10 MPa along a 4.8 mm opening and 19 cm length<sup>6</sup>.

Remedial cementing as well as lost circulation can often have situations where there is a real risk the treatment material will be cross contaminated with oil or oil mud contamination. In the case of Portland cement, the addition of a low percentage of oil mud will have a detrimental effect on slurry and cement properties<sup>7</sup>. Several experiments were conducted to look at the impact of oil and oil mud on the properties of a silicate-based plug.

Table 5 shows a AAAS:CaCO<sub>3</sub> mixed 1:1 to by weight with a 3% zinc flake slurry used as a setting agent. The oil mud was obtained from a well in Western Canada and was described as a ~85:15 with the base oil being Distillate 822. Samples were cured for 24 hours at 80C. The presence of oil mud resulted in lower amount of expansion. Decreased expansion can be partly attributed to hydrogen solubilizing in the oil. At the higher oil mud contamination there was a decrease in compressive strength. It was noted that when the 1 inch diameter by 2 inch height plug was tested on an Ingstrom® Material Tester it deformed vs. having a sharp break.

Table 5: 1:1 of AAAS:CaCO<sub>3</sub> with 3% zinc flake slurry

	% Oil Mud*	Initial Density g/cm <sup>3</sup>	Final Density g/cm <sup>3</sup>	Comp. Strength psi
1:1 AAAS:CaCO <sub>3</sub> 3% Zinc flake slurry	0	1.88	0.57	209
1:1 AAAS:CaCO <sub>3</sub> 3% Zinc flake slurry	7	1.88	0.80	210
1:1 AAAS:CaCO <sub>3</sub> 3% Zinc flake slurry	14	1.88	0.93	112

Optical micrographs were generated of different expanded silicate-based plugs. Visual observation showed a closed-cell foam. Pore quantity, shape and size were dependent on several variables including choice of bridging material. The

fly ash, Al, AAAS formulation showed >2x's expansion and consistent pore structure (figures 1a, 1b). Cell diameters were in the range of 1mm to 2 mm. As contrast a fly ash, AAAS using zinc slurry had 17% expansion with much finer pore structure (figure 2).

Where walnut hull was used as a matrix material, there was a more irregular cellular structure (figure 3). Microscopic examination shows regular sized pores within the silica gel and larger, more irregular pores developed between the bridging materials

Figure 1 a,b : Class F fly ash:AAAS expanded with Al

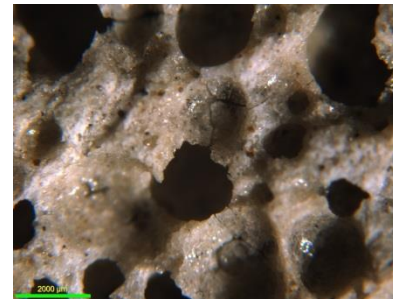
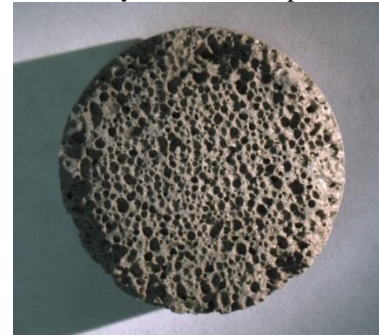
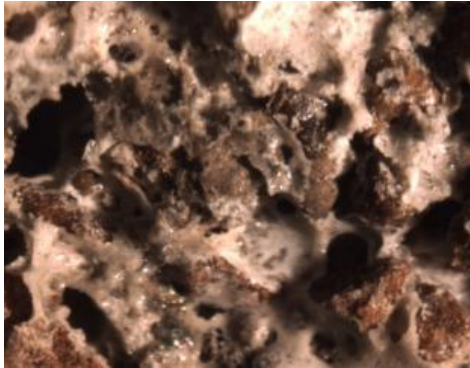


Figure 2, class F fly ash: AAAS:Fly Ash: Zn- polyethylene glycol slurry, ~ 17% expansion



Figure 3: 3.2 ratio sodium silicate, CaCO<sub>3</sub>, Walnut Hull, Zn, 10% OBM, ~60% expansion



### Field Application

Ideally, field results would have been available for presentation within this paper. A busy and very welcomed winter drilling season in Western Canada has delayed field trials until after spring break-up. This will determine the value and ease of use of this new technology.

### Conclusions

The property of expansion in Portland cement has been used for decades to improve annular sealing and prevent fluid and gas migration. Gas generating additives used in Portland cement can be adopted for use in silicate-based plugs. Existing silicate-based formulations and powdered metal technology were used as a starting point. R&D efforts also included improved forms of metal powders. Some key developments;

- zinc and aluminum can be formulated into a stable slurry
- this slurry improves handling concerns and ease of use
- the slurry can act to accelerate or retard the expansion and setting of the silicate-based plug
- volume expansion with silicate-based plugs is significantly greater than Portland cement
- a wide range of fillers/bridging material can be used in a silicate-based plug

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