ENHANCING VOID AND FRACTURE FILLING WITH AN EXPANDABLE SILICATE-BASED GROUT

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ABSTRACT

Grouting often requires a tight sealing material to fill, block and prevent communication between the isolated sections. Achieving a tight seal in a void space, fracture or crack is an on-going challenge as chemical and cement grouts often lose volume upon setting. This paper will describe the chemistry, development and application of a novel expandable silicate-based material. Similar to Portland cement, the system uses powder metals for the in-situ generation of hydrogen to make closed cell foam. In contrast to Portland cement, the silicate-based system is designed to be fit for purpose and can be formulated to expand and set from a few minutes to days. The degree of expansion can be controlled from a few percentages to five times the original volume. Final compressive strength is dependent on several factors including degree of expansion.

As a new class of material, extensively laboratory testing took place under the broad categories of HS&E characterization, formulation development, performance properties and qualitative analysis. To better focus the development effort, the geotechnical, mining and oilfield industry were consulted to determine testing and performance requirements. Industry feedback provided a wide variation in performance properties especially in the area of set times, but there was consensus in that the product needed to be safe and environmentally friendly, easy to use on-site and cost effective. This paper will provide an overview of the methodology and test results. The paper will discuss initial trial results where the expandable silicate-based plug was used in the Western Canadian oilfield to seal fractures in the reservoir. Based on lab and field results, the fit for purpose of expandable silicate-based sealant would be well suited for geotechnical applications requiring water cutoff , abandonment, and sealing of annular or void spaces.

1 INTRODUCTION

Sodium silicate based-grouts have a very long history of use for soil stabilization, and water control (Warner). As a low viscosity solution, silicates can be squeezed into soil or microfractures that would otherwise quickly bridge-off using microfine cement or polymeric material. In cases where sodium silicate is made to set by the polymerization reaction the formed silica gel can show signs of syneresis (i.e. the polymer contracts in size due to post polymerization). A reduction in volume is a concern in non-matrix environments where the objective is a tight seal. The concern with dimensional stability is not unique to sodium silicate and is known to occur in resin, polymers as well as Portland cement. One path for mitigating volume loss is to foam or expand the sealing material. Beyond creating a more dimensionally stable product there are several other benefits associated with producing cellular product;

-reduced density
-greater volume
-improved insulation properties
-improved free-thaw resistance

Portland cement has two very well established pathways for creation of cellular cement. Gas entrainment can be achieved by mechanical means where foam is created using air, surfactant and water. The produced foam is then blended into cement slurry using specialized equipment. Density is controlled by the ratio of cement to foam. This approach is commonly used for geotechnical applications such as; annular grouts for tunnels, filling of void spaces such as pipes and replacement of unstable soil under roadways.

The second approach is the chemical generation of gas. Of the various chemical reactions that generate gas, one of the oldest and still established methods is the use of aluminum as a gas generating additive. The chemistry being based on the alkalinity of the Portland cement slurry to remove the aluminum oxide surface allowing water to react with aluminum and generate hydrogen. The technology was originally invented by for structural concrete and later applied to oil well cement (Carter). Somewhat surprising, there has been little effort to use this reaction to develop a cellular silicate-based sealant. This paper provides an overview on the underlying chemistry and how the technology was first applied to fracture sealing in oil reservoirs and how the technology could be adopted for the mining and geotechnical industry.

1.1 Sodium Silicate Chemistry & Use in Geotechnical Applications

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. Two highly referenced sources of silicate chemistry and their applications are Iler (1979) and Vail (1952).

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 high pressure steam to form 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_2O. A 3.2 ratio sodium silicate can be thought of as having 3.2 kilograms of sand for every 1 kg of alkali.

$$Na_2O + SiO_2 \longrightarrow (SiO_2)_x \cdot (Na2O) + CO_2 \quad x = 1.6 \text{ to } 3.2$$

Almost all chemical, physical and performance properties of sodium silicate are determined by the ratio of SiO_2:Na_2O. The practical range of ratios produced in a furnace is 1.6 to 3.2. Geotechnical 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 silicates system is easier to polymerize and set. Upon polymerization, silica gels derived from ~3.2 ratio sodium silicate tend to provide higher compressive strengths and better durability vs. gels made with lower ratio silicates. As will be presented in the paper, the lower alkalinity can be desirable in the development of an expandable silicate-based system

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 (2013) where it was investigated as a lost circulation material in drilling fluids. As with conventional sodium silicate, the aqueous alkali alumino silicate 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.

	Na_2O (%)	SiO_2 (%)	Al_2O_3 (%)	Na_2O: SiO_2	Solids (%)	Density (g/cm^3)
AAAS	16.2	27.9	1.6	1.7	45.7	1.6
"N" 3.2 ratio	8.9	28.7	-	3.2	37.6	1.38

Table 1. Properties of Sodium Silicate Solution

1.2 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.

$$2Al_{(S)}+20H^{-}{}_{(aq)}+6H_2O \rightarrow 2Al(OH)_{4(aq)}+3H_{2(g)} \qquad (1)$$

$$Zn_{S)}+0H^{-}{}_{(aq)}+2H_2O \rightarrow Zn(OH)_{2(aq)}+H_{2(g)} \qquad (2)$$

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_2O. (i.e. 1:6 to 4.5:1). 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 $H2SiO_4{}^{2-}$ as silicate ratio increases there is a transition to $H3SiO4^{-}$ as well as H4SiO4. The $H2SiO4^{2-}$ 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.

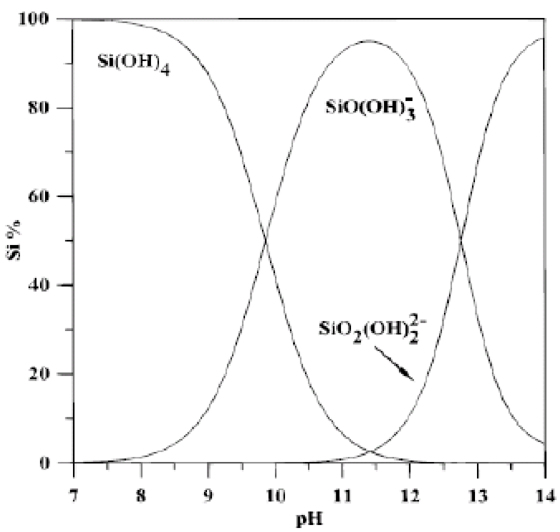

Figure 1: Distribution of silicate species at 25C as a function of pH (taken from Gout)

1.3 Other Factors for controlling Expansion Rate

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.

1.4 HS&E Characteristics

At the start of development, a review was conducted on the HS&E characteristics of an expandable silicate-based system. An objective was to maintain the desired HS&E characteristics associated with conventional silicate-based grouts. On the handling side there were initial concerns with the use of aluminum powder. As a dust, there is a potential explosive hazard if it becomes suspended in air within a explosible range. While aluminum powder is still used in oil well cements, industry has moved to the use of metals in a slurry or paste. A similar approach was taken with aluminum and zinc powders for silicate-based fluid. The engineering of a metal slurry required consideration of choice of carrier fluid and production of a stable slurry. A 25% active Zn and a 25% active Al slurry have been formulated to satisfy the HS&E safety handling concerns. Additionally, as noted, a low toxicity carrier fluid with a low freeze point was also chosen to further satisfy HS&E requirements.

Zinc is classified as a marine pollutant. While the zinc ion can be toxic, the reaction of zinc with sodium silicate not only liberates hydrogen but also serves to insolubilize zinc (equations 3). The reaction of zinc with sodium silicate serves several functions; it improves the durability of the silicate-based plug and serves to insolubilize the zinc. The 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.

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2 \qquad (3)$$
$$Zn(OH)_2 + Na2O.xSiO_2 \rightarrow Na_2ZnO_2 + xSiO_2 + H_2O$$
$$Na_2ZnO_2 + xSiO_2 + H_2O \rightarrow ZnNa_2SiO_4.H_2O + (x-1)SiO_2$$
$$2Na_2ZnO_2 + SiO_2 \rightarrow ZnNa_2SiO_4 + 2Na_2O$$

To verify the decrease in solubility and the reaction products with zinc as well as aluminum. X-ray diffraction was used to identify reaction products between sodium silicate and zinc or aluminum. Table 2 provides the base formulations along with some of the physical properties of the expanded material. Selected as a bridging material was ground soda lime glass produced from selected recycled glass cullet. In Figure 2a, the XRD analysis showed amorphous zinc silicate and no presence of elemental zinc. Similarly in Figure 2b, XRD shows no elemental aluminum with the alumino-silicate being amorphous.

	Glass Fill®	Water	Metal	Set Agent	Final Density	Comp. Streng. (24 hrs)
3.2 ratio – 50g	50 g	0 g	Zn 2.5 g	citric acid– 3.0g	0.85	25 psi
AAAS 50g	50 g	2.5 g	Al 0.2	triacetin	0.90	194 psi

Table 2: typical alkali silicate formulation

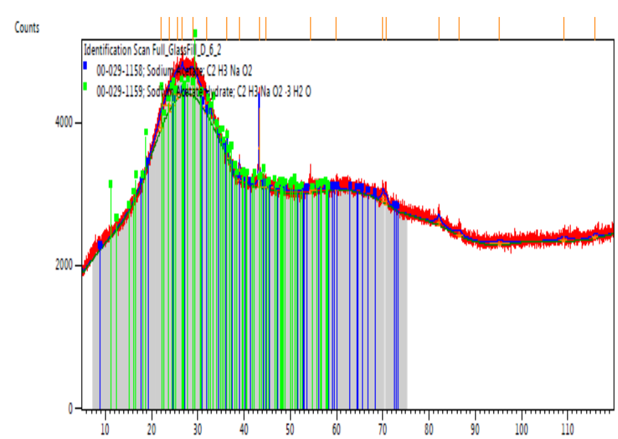

Figure 2a: XRD of 3.2 ratio sodium silicate expanded with zinc

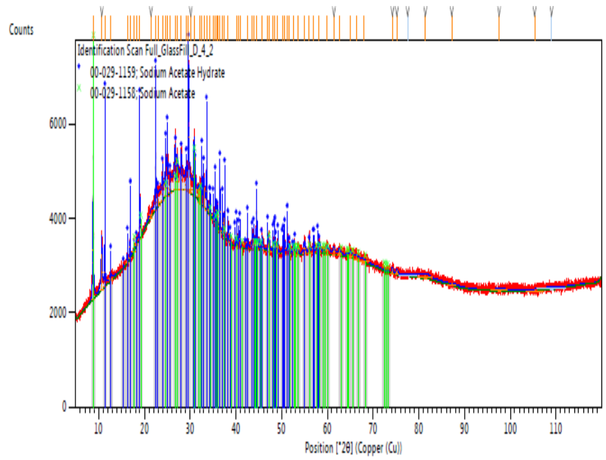

Figure 2b: XRD of AAAS expanded with aluminum

2 Development of an Expandable Silicate

Mining, oilfield and geotechnical were evaluated as starting points for the development of an expandable silicate system. All three applications use sodium silicate as a low viscosity, solids free solution for deep penetration into a permeable matrix or microfractures. This similarity was recognized by Krumrine (1985) where it was noted that technology and techniques developed for the grouting industry could be applied to water shut-off applications in oilfield. Oilfield diverges from geotechnical applications in that it will also be formulated with bridging/filler material. Commonly used material include; hollow glass spheres, walnut hulls, zeolite, diatomious earth, kaolin clay, metakaolin, glass powder, calcium carbonate, fly ash, and barite (McDonald). Of the listed bridging material, some material would be considered reactive towards sodium silicate and will give a cementitious or geo-polymer type product. Based on the presence of solids and the requirements for better sealants, oilfield was selected as the initial target application. If the technology proved successful in oil field then it would be adapted for mining and geotechnical applications.

Several oil and gas companies were consulted to better understand desired performance properties and operational requirements. Industry feedback identified several types of conformances and cement remediation challenges that would benefit from a better performing and/or more cost effective solution. A particular high value repair was fracture sealing in the reservoir. Specifically, the sealing of natural or induced fractures that provide a pathway from injection to production wells. An operator in Western Canada was looking for an alternative to cement and polymer-based technology and was interested in an expandable silicate-based sealant if it could meet the following criteria;

-set and expansion time of ~ 4 hrs. (to allow adequate placement in the fracture)
-starting density of ~1.5
-capable of withholding 22 MPa of pressure
-bridging material ~5 micron (similar to microfine cement)
-cost effective

Cross referencing existing silicate-based formulations to desired performance criteria narrowed the choice of setting agent and suitable bridging/filler material. 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 but under ambient pressure and once the formulation was finalized, it was tested using a consistiometer. Table 3 presents the developed 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. Expansion rate was calculated to be ~15%

silicate	Set. agent	filler	Expand agent	Final Density	Comp. Stren.
75 g	6 g	25 g	1 g	1.3	~1000psi

Table 3: Properties of Sodium Silicate Solution

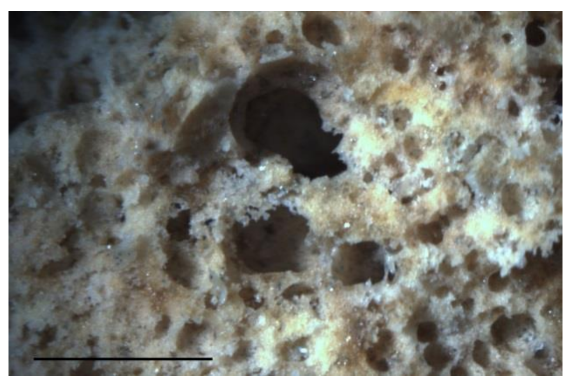

Figure 3: after expansion at 55C under 1000 psi

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

2.1 Field Trials

Two field trials were run to demonstrate desired properties and chemistry performance to effectively shut off unwanted communication in and Enhanced Oil Recovery (EOR) field (figure 4 & 5). In many oil fields EOR techniques are required to enhance well performance by increasing the amount of oil that can be produced from oil laden formations. The EOR techniques commonly used are; drilling a well that will serve as the ‘injector’ and drill other wells strategically placed that will serve as the producers. Fluids or gases such as water, CO_2, polymers, etc are injected into the injector well and pushed down the wellbore and into the formation to flood or displace the oil towards the producing wells. Over time as oil is produced, the injected fluids start communicating to the producing wells faster and faster. Those fluids/gases are reused to continuously produce more and more oil. As the oil is removed, larger and larger volumes of fluid/gasses are produced with lower amounts of oil resulting in, at some point, costs that prohibit further production of the oil by that method.

Properly treating the formation and particularly the channels that formed over time with a material that would permanently plug off the communication to redirect the injector fluids to other parts of the oil laden formation has been a challenge for many years. Many materials could be placed into the communication portions of the well bore but the challenges within the materials not being permanent nor completely and effectively filling the communication channels.

Expanding silicates are a great application for this method. Challenges with chemistry design and placement techniques restricted use of such technology but new developments as here within described in this paper now allows these systems to be placed into the formations. The unique properties of these expanding silicates allow the system to be placed and then as the reaction occurs, expansion in volume creates a better seal in the voids and to the formation rocks. High bond strength, acid, corrosion resistance and compressive strength durable enough to permanently seal off formations making it a good material in this application but also demonstrates desirable properties required in other soil stabilization and/or void-filling applications.

In the field trials, the first well was put in production approximately 1 month after treatment. Producing fluids immediately changed at producing well whereas noticeable decrease in water and gas and increase in oil production. Within almost 3 months after treatment, costs of treatment, shut in time, operational costs, etc were recovered by the increased oil production and reduced fluid production. 5 months after treatment, the trend continues with no indication of a drop in production or communication occurring. It is within our belief that should communication occur again, that it is because enough oil has been displaced and a new channel has formed.

The treatment of the second well also went excellent demonstrating the effectiveness of the designs and the stable and controllable chemistry developed. Unfortunately, other challenges with the producing well were found after treatment as they prepared to bring the producer back on line. 5 months after treatment, the producing well has come back on line and immediate results aren’t realized at this point.

Figure 3: Preparation of expandable pill

Figure 4: Pumping & placement of pill

3. Conclusion

Recognizing that industry is looking for a broader range of options, research was launched to develop compressible silicate-based slurry using gas generation additives. Technology was initially developed and field trialed for oilfield but would be transferrable to mining and geotechnical applications. 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 filler and bridging material. Initial field trials were positive and so far indicate good sealing. From a placement perspective, oilfield likely represents the most challenging of the applications as the silicate-based sealant needs to pumped and placed 1000’s of meters after preparation. Treatment zones can range from 15C to 150C or higher

In summary of the 2 field trials, it is important to note that the chemistry of this novel system is stable and has resulted in 2 challenging placement environments. The ability of this system to expand and fill into voids has largely improved the chances for success and the durable characteristics make it an excellent choice for filling voids and withstanding the tough environments it is placed.

It is important to highlight that good chemistry will go so far and problem–well diagnostics and proper placement. .are the other keys to success

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