SODIUM SILICATE AS A TREATMENT OPTION FOR CASING REPAIR AND CONFORMANCE

Mike McDonald, PQ Corporation,
Prentice Creel, P.E., T&S Petroleum Consultants

ABSTRACT

Sodium silicate has a long but somewhat overlooked history as a treatment option for conformance and remedial casing repair. Recently, there has been greater interest in the use of sodium silicate-based technology for these applications. The environmentally friendly nature of sodium silicate has been a key reason for this renewed interest. Low cost, durability and advances in silicate chemistry are the other factors driving this resurgence.

Sodium silicate is a unique chemical in that it can undergo different types of chemical reactions. This paper will review silicate chemistry and the different reactions for setting sodium silicate. The HS&E characteristics will also be discussed.

Case histories will be presented on the application of sodium silicate for blocking gas migration along micro annuli behind casing, isolating near wellbore annular fluid crossflows via channels, and step processes used to gain control over casing “pin-hole-leaks.” Also presented will be the setting reaction between sodium silicate and carbon dioxide and how it can be used for CO_2 EOR profile control and interwell communication diversion.

INTRODUCTION

Despite decades of use, sodium silicate remains a somewhat misunderstood chemical treatment for conformance. There are several reasons why silicate-based systems are not discussed with the same ease as polymer systems. The chemistry of sodium silicate defies a simple one sentence or even a one paragraph explanation. Soluble silicate appears to be a simple product made of three common components; silica, alkali and water. At a molecular level it is a complicated mixture of different size and shape molecules of negatively charged silica. These silica species can undergo several different types of chemical reactions depending on conditions and choice of catalyst. Set times can range from instantaneous to minutes to hours to days. The resulting products can range from a soft gel to a hard, cement like product. Complicating the understanding of sodium silicate is the rich lexicon of terms describing the reactions and products. This diverse terminology is a reflection of the long history of use, regional colloquialism, the use of terms imported from other industrial application and finally marketing departments trying to differentiate their company’s solution products.

Historically, there was greater interest and use of sodium silicate for conformance and remedial well repair applications. However, over the last 30+ years, polymers as well as other chemical treatments have gained in popularity[1]. The switch to polymers was partly driven by the perception that polymers were easier to use, produced an elastic gel and could be remediated if incorrectly placed in the reservoir. Concerns about reservoir damage are real when choosing sodium silicate. The highly durable, chemically resistant set of sodium silicate is a pro and a con. If improperly placed in the reservoir, the durability of a set sodium silicate is viewed as a con. For this reason, current use of sodium silicate in the Permian Basin, SE New Mexico, and other areas tends to be as a preflush for cement, loss circulation material, casing leak sealant, and for bottom-water shut off. While reservoir damage is a real concern, improvements in well and problem diagnostics as well as placement technology have helped mitigate this risk. The capabilities of sodium silicates to remediate problems generally has been shown to give a longer lasting effect, less repeat attempts, and resistant and durable results.

Over the last few years, there has been renewed interest in silicate based systems. This is seen by the increasing number of publications on silicate-based technology for conformance applications. A key driver for the increased interest is the environmentally friendly nature of silicate systems. Service companies and operators are also recognizing that they can formulate sodium silicate to be a high performances and cost effective treatment for a broader range of conformance and remediation problems. Cost of sodium silicate solutions are generally much less than polymers, in-situ polymerizing monomers, or complex chemical sealant solutions. Not all identified problems can be resolved using sodium silicates, but as a general rule, the silicate system has greater problem resolution coverage than the other remedies. An important note is that the sodium silicate solution is often co-injected with or in front of cements giving an assist to their desired implementation and final squeeze formation.

The goal of this paper is to provide the fundamentals of silicate chemistry, review basic formulations, describe their properties, benefits and methods of application. 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.

AN INTRODUCTION TO SILICATE CHEMISTRY

As stated, sodium silicate chemistry is multifaceted and defies a simple one paragraph explanation. However, key features of soluble silicate chemistry can be summarized in a page. There are several excellent papers that provide further details on silicate chemistry as it pertains to conformance. The paper by Krumrine[2] is considered a classic on the subject.

A review of the raw material and manufacturing of sodium silicate provides a foundation for describing the chemistry as well as the HS&E characteristics. Sodium silicates are manufactured by the fusing of sand (SiO_2) with sodium carbonate (Na_2CO_3) at 1100-1200°C. The resulting glass can be dissolved with high pressure steam to form a clear, slightly viscous liquid known, in many parts of the world, as "waterglass". Sodium silicate has been manufactured on an industrial scale for close to 175 years and over a million tonnes are produced annually. Major end-uses include; detergents, feedstock, pulp and paper, water treatment, adhesives and in the petroleum industry.

The most important property of sodium silicate is the weight ratio of SiO_2: Na_2O. For example, a "3.2" ratio silicate has 3.2kgs of SiO_2 for every 1kg of Na_2O. Coincidentally, the molecular weight of SiO_2 and Na_2O are so close that a 3.2 ratio silicate can also be thought of as having about 3.2 moles of SiO_2 for every 1 mole of Na_2O. Silicates are commercially produced in the ratio range of 1.5 to 3.2. The most commonly used ratio for conformance and casing repair applications is "N grade" or 3.2 ratio. As a higher ratio product, there is more silica and less alkali. This makes it easier to gel and/or precipitate. Table 1 details the properties of a 3.2 ratio.

"Silicate species" refers to the size and shape of silicate molecules found in solution. The building block for these silica species is the SiO4 monomer. Figure #1 shows a small sample of the various silicate species that can be found in a silicate solution (e.g., monomers, dimers, trimers, oligomers, chains, rings etc.). The average molecular weight of these species for a 3.2 ratio would be 280.[3] This makes the molecular weight of sodium silicate several orders of magnitude less than most polymers. The low molecular weight silica species would be less than a 1 nanometer in size (figure #2). Because of their small size, silicate can be placed deeper and with much less pressure than a polymer.

Knowing the general size and composition of the silicate molecule, one can look at the chemical reactions. Sodium silicates are unique in that they can undergo four very distinct types of chemical reactions.[3] These reactions have been defined as:

-gelation
-precipitation
-hydration/de-hydration
-surface charge modification

It is important to understand when each of the four reactions can take place in order to maximize performance, ease of use and cost.

Gelation Reaction

As shown in Figure #1, a solution of sodium silicate contains a variety of species having different sizes and shapes. These species have a negative charge which allows them to remain in solution. In order for all of these silicate species to remain completely soluble, a pH in excess of 10.7 needs to be maintained. Below pH 10.7, the low molecular weight silicate species link to form repeating bonds of Si-O-Si. The result is a silica gel. In order to initiate gelation, a sufficient quantity of weakly basic, neutral or acidic material need only be added to a solution of sodium silicate. Reaction #1 shows the polymerization of sodium silicate with sulfuric acid.

Reaction #1: Sodium silicate reaction with a mineral acid

$xSiO_2 \cdot Na_2O + H_2SO_4 \rightarrow xSiO_2 + Na_2SO_4$
x = silicate ratio (i.e. 3.2)

Note: the above reaction is used to produce the commonly seen "silica gel packet" found in many packaged goods.

Precipitation Reaction of Silicates

The negative charge on the silica molecules means that they are highly reactive with multivalent metal cations (e.g., Ca^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+}). These metal cations act as a cross linker to link together negatively charged silica (reaction #2). The resulting product is a chemically stable metal silicate precipitates. The physical properties of the metal silicate are dependent on the metal cation. For example, calcium would produce a calcium silicate, a hard cementitious material, while Mg 2+ would produce magnesium silicate, a soft talc-like product.

Reaction #2

$$-\mathrm{O}-\underset{|}{\overset{\overset{\mathrm{O}^-}{|}}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{\overset{\mathrm{O}^-}{|}}{\mathrm{Si}}}-\mathrm{O}- \;+\; \mathrm{Ca}^{++} \;=\; -\mathrm{O}-\underset{|}{\overset{\overset{\mathrm{O}}{|}}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{\overset{\mathrm{O}}{|}}{\mathrm{Si}}}-\mathrm{O}- \quad (\mathrm{O}\,/\,\mathrm{Ca}\,\backslash\,\mathrm{O})$$

Hydration/Dehydration

Liquid sodium silicate is the most commonly used form of silicate (vs. dry). In the case of 3.2 ratio product, it is 62% water. Aqueous sodium silicate can dehydrate and lose moisture to air or another substrate. As water is removed from liquid silicate, it increases in viscosity, goes through a stage of being viscous and tacky and finally becomes a glassy film. The ability of silicates to dehydrate is one of the reasons that they are so useful as an adhesive or a paint base. Under certain downhole conditions, a solution of sodium silicate will dehydrate and can provide conformance.

Conversely, a dried film of sodium silicate can rehydrate when exposed to water. As higher levels of water are removed for aqueous sodium silicate, the more difficult it becomes to rehydrate the film. Sodium silicate that has been precipitated cannot be resolubilize by water or other solvents.

Surface Charge Modification

As previous stated, the dissolved silica molecule has a negative charge. In solution, silica can donate this charge to other materials and cause them to be negatively charged. Changes in interfacial properties can cause agglomeration of particles.

SODIUM SILICATE FORMULATIONS FOR CONFORMANCE & WELL REMEDIATION

The literature presents a great variety of inorganic, organic and natural compounds that can initiate these reactions[2]. While the choice of potential of catalyst appears overwhelming, over the decades the list has been narrowed to a few proven performers. Discussions will focus on these "workhorses" and will avoid proprietary setting agents and/or application techniques. Sodium silicate is typically formulated to either undergo the gelation reaction or the precipitation. The two main categories of formulations are;

Precipitation (and generally Externally Catalyzed) – these systems are formulated to take advantage of sodium silicate reaction with metal cations (e.g., Ca^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+}). The best example of this type of formulation is a solution of calcium chloride placed in the troubled area, followed by a water space followed by a solution of sodium silicate. Once mixed, the sodium silicate reacts with the calcium to give calcium silicate.

Given that the reaction between sodium silicate and metal cations is nearly instantaneous, the catalyst cannot mixed on surface into the sodium silicate. Hence, the catalyst must be applied external of the sodium silicate. Given the quick reaction time and the limited mixing between the sodium silicate and the catalyst these systems are typically used near-wellbore. Here, a distinction is made as to the reference to near-wellbore, defined as the vugular and open portions around the well's drilled path and casings. If rapid gelation is noted, the ability to penetrate into the rocks permeability is negated.

Gelation (and generally Internally Catalyzed) – these systems are formulated with a sufficient quantity weakly basic, neutral or acidic material to reduce the pH of the sodium silicate and kick off the polymerization process. Based on the criteria of being internally catalyzed; strong organic and mineral acids would be classified in the previous mentioned category of externally catalyzed. This section will focus on weakly acidic, neutral and weakly alkaline material that can be formulated to give sufficient set times that they can be mixed at the surface into a silicate solution.

Several types of reagents have been successfully used to internally catalyze sodium silicate. The wide range of catalysts also results in a wide range of set times and properties. It is also possible to run a mix of different catalysts. This versatility allows for use in several different types of conformance problems. From the very extensive list of potential catalysts and catalyst combinations the bulk of conformance applications can be formulated from a dozen or so standalone, garden variety catalysts. This is not to say that the research is stagnant of new developments of improved catalysts for silicate. A recent example of such research is biocatalyzed silicate gels[4].

The longer reaction times take advantage of the low viscosity (Table 2) and low molecular weight for deep placement in the reservoir. Distances of penetration are variable from within several feet to extended distances. The penetration will always be conditional on variations of high permeability to lower permeability arrays. If leeched out permeability exists, the indications will be that the sodium silicate will gain deepest penetration within these less tortuous paths. Regardless of the tortuosity, sodium silicate gels will penetrate much deeper than polymer gels with their fibrous mass, due to silicate's initial pre-in-situ gelled, low molecular weight.

Both the externally and internally catalyzed systems can be formulated to include other material besides water and a catalyst. The addition of additives can improve performance, provide better control over set times and/or reduce cost. Care must be taken to determine if the choice of additive will impact the set time for internally catalyzed silicate systems.

Fillers & blocking material – sodium silicate has the capacity to carry fillers and blocking materials. Sodium silicates are used as the base fluid to create slurries when they are mixed with materials such as sand, finely ground sand, micro sands, and "silica flour", crystallized co-polymers, calcium carbonate, zeolite, diatomaceous earth, etc. These additions allow for the formation of a cementious mass that is more capable of blocking mixtures provide catalyzed solid slurry capable of building a cementious mass and fill large volumes such as; loss circulation, near wellbore voids, vugular fractured channeling features and fracture sealing. [5, 6]

Polymers – sodium silicate has commonly being combined with a variety of different types of polymers[2]. The use of polymers helps to broaden the functionality of silicate based systems and improve physical properties such as gel brittleness and syneresis.

TREATMENT, PLACEMENT AND JOB EXECUTION

Prior to selecting and formulating a sodium silicate-based system, thorough diagnostics are required to determine what may or may not be happening in the reservoir. Once problem identifications addressing conditions and performances in production and/or injection are quantified and qualified, a determination can be made if sodium silicate-based solution is the best technical and economical solution to modify reservoir conditions.

Often times, the diagnostics being performed to determine the problem(s) may also be utilized to determine the applicable placement technique to best address the cause of poor performance in production. Given the chemical durability of silicate-based solutions additional care is necessary to properly place the material in the most advantageous portion of the reservoir. Simply dumping in or squeezing sodium silicate or any other conformance chemical in a well and justifying placement on a possible misleading pressure response has led to the reported failure of Conformance Treatments at 70-80 percent.

Historically, when proper diagnostics are used in the process of "Problem Identification", "Best Solution Selection Method", and using a proper "Placement Technique" to solve the poor injection or production performance, desired results have been achieved. Most failures in obtaining a successful result can be attributed to not applying a diagnostically determined "Best Placement Technique." Proper placements have shown to improve results from the norm of 30 percent up to 85-95 percent success. [7, 8, 9]

Sodium silicate-based formulations can be less forgiving than polymer systems and a higher level of job execution and onsite knowledge is required to insure the proper placement. The industry needs to recognize the requirement to have this understanding to utilize the available tools and knowledge gained from history and past performance of these treatments. Focus should start from the beginning to understand what cause and effect may be giving less than desired production or injection performance in the reservoir, to develop superior products and methods to address a varied and wide requirement, and to design and interpret the placement of these solutions for enhance production. A synergistic approach is best to meet these goals. [7, 8 9, 10, 11]

GENERAL USE OF SODIUM SILICATE IN THE FIELD & OPERATIONAL REQUIREMENTS

Handling sodium silicate in the field in transports and mixing/pumping equipment requires an environment that is low in dissolved metals and/or acidic material. Equipment is always cleaned and flushed with fresh water or oil prior and post handling sodium silicate. Proper pumping placement of sodium silicates is performed in step stages whereas the silicate is surrounded with fresh water when injecting down tubulars. Purpose is to not encourage a reaction until the sodium silicate is introduced into the annular portion where the squeeze is desired. Likewise, when injecting sodium silicate internally catalyzed systems for deep penetration on conformance treatments, fresh water pre-flush of significant volume to flush away any external reaction catalyst is important.

Field operations require internal catalysis to be mixed into the sodium silicate solutions just prior to injecting the material. The mixing, blending, and placement time is added to the set time to allow for placement control. Based on the catalyst used and the final placement temperature, the amount of catalyst added to the mix is tested per laboratory analysis using the mix and the selected catalyst that will be used. Based on complexity of the treatment and the desired set time, internally catalyzed sodium silicate solutions are often streamed together in calculated ratios from component tanks providing the silicate and the catalyst. This method is highly important for offshore operations with limited space and facilities.

Operations whereas an external catalyst will be used to trigger the reaction, placement steps with fresh water pre-flush and post-flush are still required. The placement and squeeze occurs following a reaction time once the silicate comes into contact with the external catalyst such as a brine or acid.

Conformance options in placement are varied and based on the desired reaction during the injection process. Techniques such as placing either external or internal reacted sodium silicate followed with a small fresh water spacer and then by a volume of acid will produce a squeeze and then diversion into another portion of a formation. The shut off of water production and stimulation into another more productive interval can be achieved in this technique. Other techniques in placement are as varied and should be always based on an understanding of the diagnosed reservoir conditions and production or injection problems. [10, 11]

BLOCKING GAS MIGRATION

Given the importance and increasing public awareness of issues with surface casing vent flow, this application was selected for review. Almost all regulatory bodies require no gas leakage at the wellhead prior to cutting and capping at well abandonment. Continued daily operation of wells also requires annual or other regulatory time interval testing to show no gas to surface indications. Surface casing vent flows and gas migration are becoming increasingly difficult and expensive to repair.

Sodium silicate is used in the Permian Basin and SE New Mexico to block channels behind casing. Often, micro fractures and fissures in casing annuli are extremely tight making it very difficult to squeeze into and block gas migration. Cements, XL gels, and even micro fine cements cannot gain entry due to their size and viscosity. A slight dilution of sodium silicate with water will give a viscosity close to that of water. The less than nano size of sodium silicate molecules also allows easy and deep placement in channels.

Usually conditions in the casing annulus are such that the precipitation reaction will be the dominant mechanism of setting for the squeezed sodium silicate. Typically channels are rich in calcium ions existing in the original primary cement. [10] Conditions also allow for the gelation and dehydration of sodium silicate. Should the venting gas contain CO_2 there will be a gradual reduction in pH and the initiation of polymerization.

Each repair design is unique, in simpler cases water/sodium silicate solution is sufficient to block channels. More severe problems involve the use of bridging and/or setting agents with sodium silicate.

The size and the extent of channels are the major factors that dictate the formula. Other factors include;

- -make-up of gas (i.e. CO_2)
- -set time
- -pumping strategy (expected feed rates)
- -depth,
- -pressure
- -downhole temperature

Concentration can vary from very dilute (5% to as is). As a rule of thumb;

- -the higher the silicate concentration, the greater the strength
- -higher the silicate concentration equals less syneresis
- -the quicker the set, the greater the final strength
- -high concentrations are much more difficult to catalyze internally
- -the incorporation of salt will help accelerate gel times

SILICATE-BASED PACKER FLUIDS

Sodium Silicates are excellent packer fluids and have historically shown tremendous benefits when used to protect annuluses of tubing to casings and casings to casings from corrosion and pressure build-ups due to failures in the outer casings. The efficacy and mechanisms of corrosion control well are established and have been detailed by McDonald [12]. The sodium silicates are generally blended at 5% to 20% of a fresh water base and are gelled with proprietary activators. Historically, total protection from corrosion has been achieved for over 60+ years as indicated when casings have been pulled during plugging operations. Often packer fluids are produced by blending sodium silicates with silica flour producing a slurried mass. The capability of providing a ready-made squeeze material, if placed in wellbore annuluses to address outer casing leaks if occurring, saves time and costs to repair.

CASING REPAIR

Repairing casing pitting or corrosion pinhole leaks has become a priority to many operators. These repairs are required on injection wells to satisfy regulatory tests and on producing wells to stop unwanted production. Casing leaks can occur in designated freshwater zones, across intervals with poor original primary cement jobs, or in intervals with a high influx of water. If the casing leaks on injection wells are not successfully squeezed and fail regulatory testing, the operator may be fined and the wells may have to be plugged and abandoned. The influx of unwanted water into producing wells with pinhole casing leaks can cause formation damage, loss of production, and can greatly increase the corrosion of tubulars and surface equipment. Many of these leaks are so small that even small-particle cement cannot be placed outside the casing to build a barrier to the water influx or to obtain zonal isolation. The initial liquid solution demonstrates unique capabilities for squeezing tight casing leaks with high success. [5, 6, 10] As shown in Figure 3, these casing “pin-hole-leaks” are addressed using the external catalyzed method and staged with hesitation squeezes. Sodium silicate gels form particulate solids when the solution contacts divalent ions such as calcium, an internal-activating catalyst, or cement. Formation of particulate solids causes a paste to build up when the water phase is squeezed from the solution. This paste-like material continues to build up during the squeeze process until it forms a permanent solid that has strength equal to the final squeeze pressure applied. The final squeezed mass, which through the continued squeeze effort affects the carrier fluid loss, actually gains extremely high compressive strengths, and remains stable. The mass acts as both a shut off from external pressure and internal pressure losses. The process develops a compressed and solidifying mass capable of sealing off extremely small leaks and protecting casings. This technique has been employed for over 70 years to help meet regulatory requirements on annular pressure build-ups. Other squeeze methods require much larger amounts of sodium silicate [internally set] to resolve the annular problems such as long intervals with virtually no cement integrity and influx flows exist. Figure 3 also shows this technique.

Combining sodium silicate with fillers such as silica based solid materials, fiber-like strands, swelling crystallized co-polymers, and product wastes from such manufacturing entities as Formica has evolved to solve specific difficult identified problems. [13] Often needed is the high strength, solidifying mass and physical changes in the components along with the gelation of the sodium silicate to develop a solution capable of addressing these dynamic problems. [5, 10, 11] Sodium silicate solutions with either fine sodium silicate flour or coarse sodium silicate flour added to create slurry also can be used to squeeze casing leaks where a greater test-pressure drop vs. time is encountered. Statistics were gathered to allow engineers to gauge the pressure-drop ranges where variations in amounts of silica flour (slurry density) and sizes (fine vs. course) could be chosen to squeeze leaks. Since the silica flour is not a factor in set-time development, its use would be to give additional leakoff blockage, providing surface area on which the squeezed particulate could develop.

As mentioned in the field use and operational requirements section, sodium silicate is often injected as a diverter and squeeze material for zonal isolation while initiating entry into a previous un-produced interval or injected segment when combining the treatment with an acid. The reaction of acid when combined with sodium silicate will cause the solution to set into a fairly sufficient diversion mass capable of reducing injection by several hundred psig. This blocking and diverting process has been used to address bottom water cone-ins on producers and profile modifications on injectors. [10, 11]

CASE HISTORY #1: REPAIRING LEAKS IN PRODUCTION CASING

In the past, many operators located the leaks, set retrievable bridge plugs to protect the production zones, and cement-squeezed the leaking interval using composite or cast iron cement retainers. If possible, the operators circulated cement up to the surface if annular channels exist to help eliminate future problems. The problems associated with this method were casing integrity, heaved-in annulus sections, and hydrostatic restrictions of exposed formations. Typically, these problems are associated with wells that have a crossflow of water from a shallower zone down the annulus into a porous interval that would accept fluid because the hydrostatic pressure was greater than the reservoir pressure.

As an alternative, sodium silicate solutions have been used on wells where these water leaks have occurred. Placement of the sodium silicate solution into the annulus is easily achieved even when it is difficult to inject leaking intervals. The service companies chose the volume to run based on the pressure restrictions. The gelled formation of the sodium silicate solution seals off the leaks and provides a very economical alternative to conventional squeeze methods. Usually the jobs do not require squeeze packers or retainers if casing integrity above the leak is satisfactory. Retainers have sometimes slipped and often cause penetrated holes in the old casings from the protruding slips on the tools. Once a placement and squeeze attempt is made, the remaining sodium silicate solution inside the casing is removed with the tubing used to spot the solution and is circulated out of the casing. This procedure helps eliminate the drillouts associated with cementing and also helps reduce the chance of damaging the old casings with a drill bit.

CASE HISTORY #2: REPAIRING AN INJECTION WELL THAT HAS A LEAK IN THE CRITICAL ZONE

A state regulatory commission authorized this squeeze to be performed on an injection well that had a regulatory requirement addressing a leak occurring within its "critical interval" (400 to 800 ft and considered a freshwater zone). The squeeze was allowed because the sodium silicate solution was intended for permanent placement. This was based on the capability of the sodium silicate squeezed solution's capability to stand up under the zones environment for an exceptionally extended time. Also considered, was the fact that the fresh water interval already consists of water containing silica as all water does. The area was specified as a freshwater zone from ground surface down to 1,250 ft. Three previous squeezes with conventional cementing methods had failed and testing indicated that no cement was being placed into the leak, only built up inside the casing as nodes on the inside face of the casing where the leaks existed. The follow-up drillouts of the cementing squeezes resulted in the same pressure leak even though the cement had been squeezed up to 1,000 psi.

The well test pressure falloff rate was at 450 psig/h. This was started at an initial test pressure of 500 psig before and after the cementing squeezes. The only regulatory requirement was that the operator would have to perform a repeated pressure test every 12 months instead of every three years. If the pressure test was successful, the operator could perform another pressure test in 2 years and continue follow-up tests every 3 years. The operator possibly could have used ultra-fine-grind cement on this well, but because of past failures with fine-grind cement at this depth and the costs associated with this procedure, the operator chose to try the sodium silicate solution.

Because of the rapid pressure drop [450 psig/hr.], the operator had to squeeze the well twice using 750 gal sodium silicate each time. The volume of sodium silicate solution placed in the well to perform each squeeze was based on the capacity of the casing from 800 ft up to 50 ft from the surface. The first attempt caused the pressure to drop from the initial pressure loss of 450 psig/hr. to 150 psi/hr. The well also would not drop below 350 psig, holding steady at this pressure. On the second attempt, a squeeze of 1,000 psi was reached with a holding pressure of 600 psig after a decline over 3 hrs. This pressure was deemed satisfactory since it was higher than the 500 psig required by the 12-hour regulatory test. The sodium silicate solution would only hold the 600-psig pressure level because of the compressive strength of the rock and salt formation surrounding the wellbore at the 400-ft depth. The well has continued to pass the three year scheduled tests since the sodium silicate squeeze done in 2001.

CASE HISTORY #3: ADDRESSING AN INTER-WELL THIEF ZONE

During a field wide development for in-fill injection wells, the operator discovered that on all of the newly drilled and completed injection wells, a carsted extremely high permeability thief zone would be encountered. This interval lay centered within the main pay zone and was capable of being picked out on open-hole logs. Based on other injectors within the field unit, injection profile analyses indicated these older wells also had the carsted interval and almost 100% of injection was entering it. The carsted interval averaged less than 10 ft in height on the wells. These carsted intervals are noted in the prolific and generally water and CO_2 flooded San Andres formation in the Permian Basin of West Texas and SE New Mexico.

The operator chose to be pro-active in addressing this anomaly by treating with a blocking conformance agent as a first step in the well's completion. The intervals would not be beneficial in injection and would most certainly give a rapid breakthrough to offset producers. Cycling water injection within this unit via the carsted intervals has been addressed in the past, but normally done after years of injection and poor performance. Difficult and costly procedures were done to address the thief intervals using complex treatments and complicated placement techniques. When all the desired injection intervals are open and stimulated, squeezing off a specific interval and not damaging injection into the other intervals can be chancy.

The operator chose to shoot the carsted interval first and treat with a large volume of sodium silicate water blend solution containing an internal activator. The designed pump time was for placing the treatment deep into the formation. Mixing, activating, and placement was done over a 14 hour period with the injection rate designed to stay within the carsted interval and not exceed a pressure limit that would cause a leak-off into the pay above and below. Treatments for 60+ wells were performed as wells were drilled with great success in shutting off these carsted thief intervals without doing any damage to the desired pay for injection. Later profile analysis through the next 25 years has shown that inter-well breakthrough is minimal on these wells.

CONFORMANCE FOR CARBON DIOXIDE EOR

Sodium silicate represents a potential elegant method for blocking and controlling the placement of CO_2 for enhanced oil recovery. CO_2 is readily soluble in solution and yields a weak acid that permits sodium silicate to be gelled at a controlled rate to yield a silica gel. This chemical reaction is well understood and has been used extensively by the foundry industry for over 50 years for making cores and molds. The chemistry along with the properties, benefits, limitations and methods of application have been well documented by the foundry industry. [14]

$$Na_2SiO_3 + H_2O + CO_2 \qquad Na_2CO_3 + SiO_2\,\text{(gel)} + H_2O$$

While far less developed, the idea of setting sodium silicate with CO_2 has not been lost on the petroleum industry. In 1946, a US patent titled, "Method of Oil Recovery" describes the use of sodium silicate with CO2 to modify reserve permeability. [15] Sodium silicate is selectively place into a high permeable zone. Carbon dioxide is then injected into the same zone. The patent notes that a silica gel is formed but attributes the permeability modification to the development of viscosity; a large viscosity coefficient reduces flow to negligible (per Darcy's Equation)

$$Q = \frac{KA(P_1 - P_2)}{uL}$$

where
Q=flow in unit volume per unit of time
K=Darcy's constant (permeability)
A=unit area
P_1-P_2=pressure drop along unit distance
u=coefficient of viscosity
L=length

Researching a historical data base on remediation and conformance work done over the past 60 + years, references were noted as to the use of sodium silicate as a near wellbore squeeze material for mitigating CO_2 behind casing annular migration and its detrimental effects caused by the carbonic acid produced. Other references were noted on placing internally catalyzed sodium silicate solutions into inter-well high permeability communication thief zones for diversion of injected CO_2 (profile modification) and blockage of CO_2 inter-well breakthroughs [9, 10]. A recent paper by Laktos documents the use of sodium silicate/polymer/urea as a method for restricting CO_2 migration in and around a collapsed well [16, 17, 18]. The polymer served to increase gel flexibility and limit the degree of syneresis. Urea was used to assist as a catalyst.

HEALTH, SAFETY & ENVIRONMENT

To complete this paper, a snapshot is given of the health, safety and environmental performance of silicate-based systems. Sodium silicates are derived from, and ultimately return to nature, as silica (SiO_2) and soluble sodium compounds. Since these are among the earth's most common chemical components, they offer minimum potential for harmful environmental effects and contribute to the natural silicate pool found in water, earth and plants. Natural silica similar in composition to silica from sodium silicate is found in river water at concentrations ranging from 5 to 35 ppm dissolved silica[3].

The benign nature of sodium silicate is reflected in various regulatory approvals as well as end-uses.[19] The FDA has classified sodium silicate as GRAS (Generally Recognized as Safe) for a number of food-related uses.[19] The EPA allows the use of sodium silicate as a treatment option for numerous potable water applications (i.e. corrosion control, treatment of red water). Given that sodium silicate is deliberately added to potable water, there is minimal risk for its use in fresh water intervals.

The main hazard associated with soluble silicates derives from their alkalinity.[18, 19] The typical sodium silicate used for conformance applications is considered moderately alkaline. To put the level of alkalinity into perspective, it would be similar to many household powder laundry and automatic dishwashing detergents. These products typically contain a significant percentage of sodium silicate. Silicate may cause minor skin and eye irritation depending on the degree of alkalinity and exposure time[19]. Thus, use of protective clothing along with Personal Protective Equipment (PPE) is strongly recommended.

CONCLUSIONS

1. Field results indicate that sodium silicate can be used to solve numerous conformance problems.
2. There is increased interest in sodium silicate based technology that is being driven by the need for environmentally friendly solutions.
3. The potential exists for sodium silicate to be an effective treatment option for CO_2
4. Pinhole casing leaks can be successfully repaired by using sodium silicate gel solutions.
5. Sodium silicate solutions are highly effective in filling and providing integrity for near-wellbore regions. An additional feature is the sodium silicate solutions may be used with fillers, slurried with silicate solids, and provide unique characteristics as carrier systems.
6. Sodium silicate solutions provide a varied means of providing deep formation fluid diversion and have been used more than any other system for profile modification. The ability to provide stable and effective controls for inter well high permeability communication to dynamic fracture short circuits within producers and injectors has been demonstrated in past workovers for over 60+ years.

REFERENCES

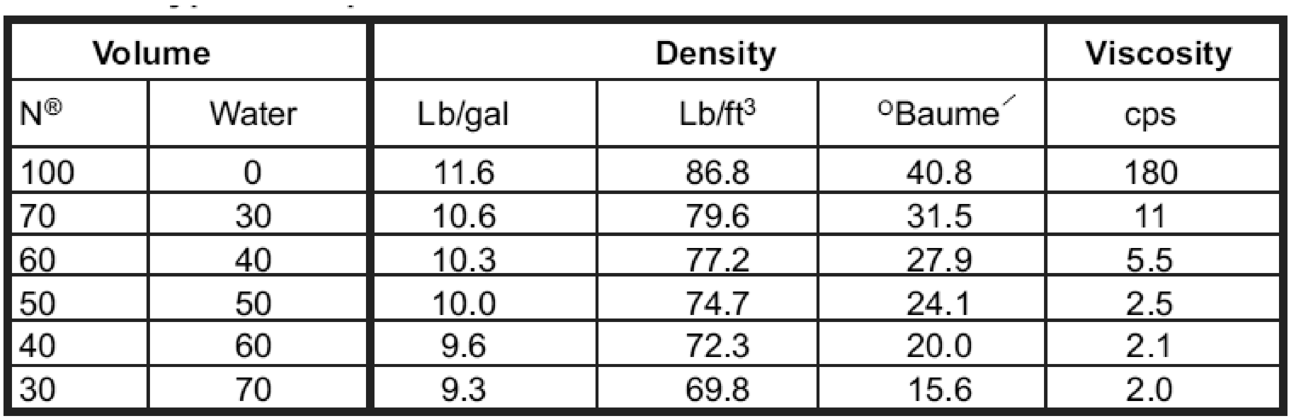
1. L.D. Burns et. al, "New Generation Silicate Gel System for Casing Repairs and Water Shutoff", SPE 113490, SPE Improved Oil Recovery Symposium, Tulsa, OK, April 19-23, 2008
2. P. H. Krumrine and S.D. Boyce, Profile Modification and Water Control with Silica Gel-Based Systems, SPE 13578 presented at the 1985 SPE International Symposium on Oilfield and Geothermal Chemistry, Phoenix, AZ, April 9-11, 1985
3. Iler, R. K., "the Chemistry of Silica", Wiley-Interscience, New York, NY, 1979
4. S. Falkowicz et al., "Biocatalized Silicate Gels in Oil and Geothermal Industry", Gospodarka Surowcami Mineralynymi, Tom 25, 2009, zesyt 4
5. Creel, P & Crook, R. "Pinhole Casing Leaks Successfully Repaired with Sodium Silicate Gel Solutions and In-Situ Polymerizing Monomers in Squeeze Operations," Twelfth Oil Recovery Conference, Tulsa, OK, March, 1997.
6. Smith, C.W., Pugh, T.D., and Mody, B.: "A Special Sealant Process for Subsurface Water," paper presented at the 1978 Southwestern Petroleum Short Course, Texas Tech University, Lubbock, TX, Apr. 20-21.

7. Soliman, M. Y., et al.: “Study of the Effect of Early, “Technology Integration on Conformance Problems and Solutions,” presented at the 5th International Conference on Reservoir Conformance, Profile Control, and Water and Gas Shutoff, Houston, Nov. 8-9, 1999.
8. Soliman, M. Y., Creel, P., Rester, S., Sigal, R., Everett, D., and Johnson, M., SPE 62553, “Integration of Technology Supports Preventive Conformance Reservoir Techniques”, 2000 SPE/AAPG Western Regional Meeting, Long Beach, California, 19–23 June 2000.
9. Creel, P.G., Garvin, T.R., Carlisle, B., Pappas, J., Hirth, B., Comer, L.,: "Database assemblage of Engineer's Reports, Treatment Designs & Performances, Diagnostic and Analysis Data, Post Treatment Appraisals, and Operator's Evaluations on Conformance Treatments in the Permian Basin, West Texas (1965-1998)," paper and presentation at the MoBPTeCh* Produced Water Management - Best Practices for the Permian Basin, Midland, TX., November 17 & 18, 1998. [*Mobil, BP, Texaco, & Chevron]
10. Dalrymple, D., Sutton, D., Creel, P. G.: “Conformance Control in Oil Recovery,” paper presented at the 1985 Southwestern Petroleum Short Course, Texas Tech University, Lubbock, Texas, Apr. 24-25.
11. Creel, P & Booker, J, “Correcting Out-of-Zone Injection Problems on a Waterflood in SE New Mexico, #200731, 54th Annual Southwestern Petroleum Short Course, Lubbock, TX, April 25-26, 2007.
12. M. McDonald et al., "Use of Silicate-Based Fluids to Mitigate Corrosion”, SPE 100599, 2007 SPE International Symposium on Oilfield Chemicals, Woodlands, TX, March 2007
13. Laboratory Analysis Investigations and Reports on Sodium Silicate as Transport Fluid for XL Crystallized Co-Polymers, Baroid, Houston Technical Center and Halliburton Laboratory Facilities, Odessa, TX, May 1998, April 2000, July 2002, Sept. 2004, November 2006.
14. D.V. Atterton, The Carbon-Dioxide Process, 56-162 presented at the American Foundrymen’s Society, Atlantic City, NJ, May 3-9, 1956
15. US patent 2,402,588, 1946 - Method for Oil Recovery, Kurt H. Andresen, Bradford, Pa., assignor, by mesne assignments, to Essex Royalty Corporation, New York, N.Y., a corporation of Delaware.
16. Lakatos, I. et. al, “Prevention of Vertical gas Flow in a Collapsed Well Using Silicate/Polymer/Urea Method,” SPE 121045, International Oilfield Chemical Symposium, Woodlands, TX, April, 2009
17. Cole, C. and Lindstrom, K.: “Well Integrity Maintenance Using Pumpable Sealants,” paper presented at the Underground Injection Practices Council International Symposium, New Orleans, LA, May 1987.
18. W. L. Schleyer, J.G. Blumberg, “Health, Safety, and Environmental Aspects of Soluble Silicates.” The 1982 American Chemical Society
19. FDA, SCOGS-61 “Evaluation of the Health Aspects of Certain Silicates as Food Ingredients.”

Table 1
Properties of a 3.2 ratio Liquid Sodium Silicate

Product	Wt. Ratio SiO_2/Na_2O	% Na2O	%SiO2	Density g/cm3	pH	Viscosity Cps	Characteristics
N®	3.22	8.9	28.7	1.38	11.3	180	Syrupy liquid

Table 2
Typical Properties of Diluted 3.2 ratio Sodium Silicate



Volume		Density			Viscosity
N®	Water	Lb/gal	Lb/ft^3	°Baumé	cps
100	0	11.6	86.8	40.8	180
70	30	10.6	79.6	31.5	11
60	40	10.3	77.2	27.9	5.5
50	50	10.0	74.7	24.1	2.5
40	60	9.6	72.3	20.0	2.1
30	70	9.3	69.8	15.6	2.0

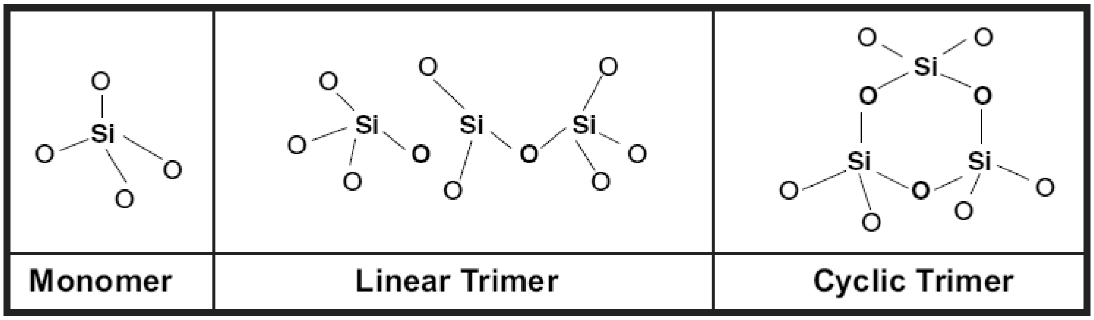


Figure 1 - Small sample of the various silicate species that can be found in a silicate solution

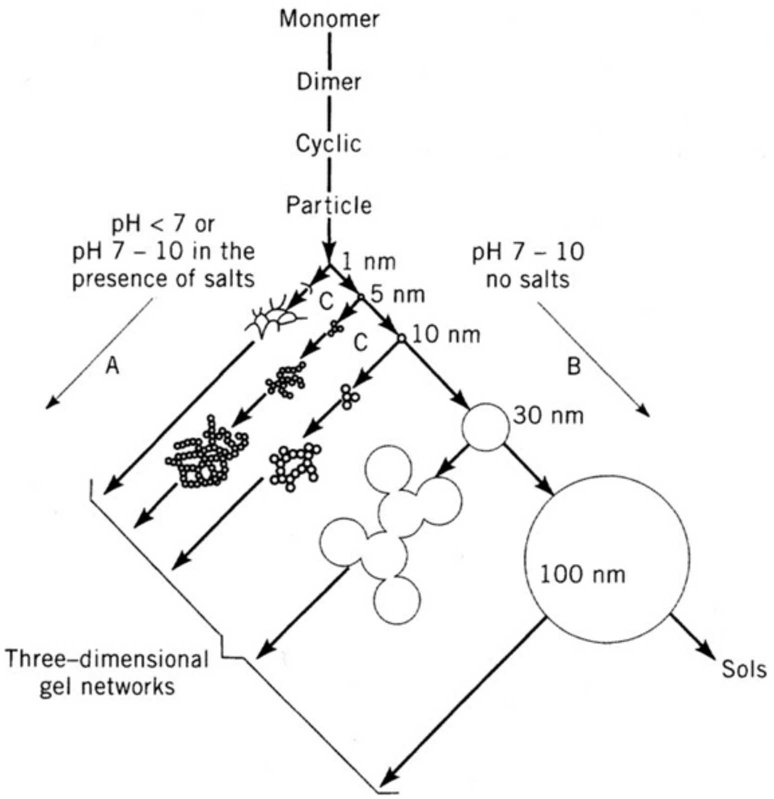


Fig. 2. Schematic representation of the polymerization of monosilicic acid (9).

Figure 2 - Properties of a 3.2 ratio sodium silicate

Figure 3 - Example of squeeze on “Pin-Hole-Leaks: