

HIGH-TEMPERATURE PLUG FORMATION WITH SILICATES

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ABSTRACT

A grouting system is being developed that is applicable to water shutoff, steam flooding, and high-temperature grouting/plugging for lost circulation. This grouting system uses silicate hydrates as the plugging material. We describe a means to introduce sodium silicate and an activator through a single tubular by encapsulating the activator in a material that is temperature sensitive, thus delaying the initiation of the reaction. The formation of silicate hydrate plugs has been studied over the range of 80°C to 300°C as well as the chemical stability of silicate hydrate for 10-12 weeks.

INTRODUCTION

This work describes a chemical solution of exploiting silicates' unique gelling properties in an environmentally friendly and cost-effective way to form plugs for use in water shutoff strategy, steam flooding, and high-temperature grouting/plugging for lost circulation. Silicates have been used to form stable grouts and cements for over 50 years because of their ability to gel and polymerize. This reaction has also been used successfully for water shutoff and to solve lost-circulation problems in oil and gas drilling that require a plug to be formed at various weak spots in a well formation. The reaction happens in seconds to minutes (generally controlled by the mixing rate). In addition to their gelling action, silicates will also react with soluble metal salts, such as calcium chloride, to produce insoluble metal silicate hydrate plugs.

The need for this work arose primarily from geothermal drilling research wherein we are faced with severe lost-circulation problems, often at elevated temperatures. This paper summarizes current laboratory-based advances in developing high-temperature plugs for lost-circulation zones. The purpose of this research includes developing emplacement systems and determining the temperature limits of reactive plugs for cross flow. Sandia National Laboratories, with support by the Geothermal Technologies Program of the U.S. Department of Energy has studied wellbore integrity in geothermal environments. A portion of wellbore integrity research has been directed towards developing materials and methods of solving lost circulation problems in a cost-effective way. Geothermal environments are hot, with temperatures in the range of 80°C to 300°C, and are possibly laden with water, brine, etc. In severe lost-circulation situations, cross flow may be experienced, in which pressure-induced fluid flow may occur through a borehole. When lost circulation of drilling fluid is experienced in geothermal wells, cement plugs are a common initial solution to the problem. A typical procedure would be to stop drilling, place the cement plug and allow the cement to cure, and then re-drill. However, high cross-flow rates and/or large voids, many fractures, and high porosity/permeability zones can present difficult circumstances for conventional cement plug deployment. For example, cement can be washed out or migrate away from the zone of interest due to unbalanced hydrostatic pressures before it has set, or the amount of placed cement may not fill all of the voids present.

As background, lost circulation occurs when formation-fluid pressure is less than the fluid column pressure in the wellbore, so that some or all of the

drilling fluid escapes into the formation instead of recirculating back up the well annulus. Lost circulation is often accompanied by further loss of wellbore integrity including sloughing, caving, washing out, or bridging. These phenomena are persistent in geothermal drilling and are very expensive – often accounting for 10-20% of the total cost for drilling a typical geothermal well – and cause many additional drilling problems such as stuck drill pipe, damaged bits, slow drilling rates, and collapsed boreholes.

Lost circulation is particularly difficult to plug when it includes cross flow. Cross flow occurs when the wellbore encounters permeable zones whose pore pressures are not hydrostatically balanced (Figure 1). This often occurs when alluvial deposits are separated from underlying volcanics by an impermeable layer. The fluid level in the borehole may fall hundreds of feet below the surface (significant lost circulation/cross flow) when drilling penetrates the volcanics. Therefore, if the surface casing shoe is not set in the impermeable zone, the well can have cross flow from one zone to another sufficient to wash away all cement plugs and primary cement.

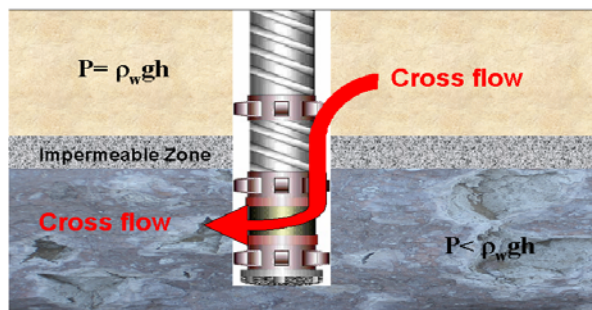


Figure 1: Cross flow occurs when two formations have unbalanced pore pressure (P), where ρ_wgh is the weight of a water column back to surface.

For a geothermal short circuit, water shutoff and to control flow in steam flooding, the problem is slightly different. In these situations, the grout must flow into fractures or into a permeable zone, filling it, and set up in an intelligent manner to affect a seal. This concept implies that timing or reactivity of the plug material must be considered as part of the grout system.

We envision a system which works as follows. When a loss zone is encountered, the drilling would be stopped and the drill string backed off one to two stands. A reactive grout material would be injected through the drill string to the hole bottom and allowed to flow into the loss zone and the immediate

vicinity. There it would react, gel/harden quickly, and allow for continued drilling almost immediately.

In order for this concept to become functional, we have been studying reactive plug systems for geothermal (hot and wet) environments.

Through a systems approach, we are investigating materials that can be created and will survive in a geothermal environment without degrading. The chemistry as well as the “mechanical survivability” of the materials at geothermal conditions has been studied, initially through lab and planned bench-scale and field-testing. Awareness of a reasonable downhole deployment scheme must be factored into early material development work. Materials considered must be environmentally suitable and the total costs of the material’s deployment process must be economic, realizing that down time caused by lost circulation is very costly.

Recognizing the importance of minimizing trouble time caused by severe lost circulation in geothermal wells, we have studied the chemical stability of potentially viable silicate plugging material. The material satisfies multiple needs, namely: (1) no special handling requirements and considered non-hazardous by the DOT and EPA; (2) low cost (3) readily pumpable; (4) controllable gel time- the reaction rate needs to be adjustable for varied conditions both at the surface and downhole; (5) controllable placement such that it has minimal water solubility and adheres well to rock surfaces through a single delivery hose; (6) hydrothermally stable for 8 weeks at geothermal temperatures; and (7) once placed, the grout is sufficiently stiff, to allow drilling with conventional means, and no unanticipated problems with drill bit plugging. These criteria were used because the initial situation we wished to address was that of geothermal lost circulation.

SILICATE CHEMISTRIES STUDIED

Silicates have the ability to polymerize and form gels, or plugs, with other chemicals. Several chemicals were screened for their plug forming ability with silicates. The stability of these plugs was studied at temperatures of 25°C to 300°C.

Water shutoff and lost circulation (Heaven et al, 1999; Lakatos et al, 2001; Samari et al, 1998; Viddick et al, 1988) applications require a plug to be formed at various weak spots in a well formation. Silicates are very stable and do not have the adverse environmental effects associated with other gel-forming chemicals (Heaven et al, 1999; Lakatos et al, 2001; Samari et al, 1998; Viddick et al, 1988). Soluble silicates contain three components: silica, alkali and water. Although silicates have been described as the metal salts of silicic acid, they

actually exist as polymeric forms in solution. The fundamental building block of silicate solutions is the silicon atom at the centre of an oxygen-cornered, four-sided tetrahedral pyramid (Figure 2). In sodium silicate, typically, each oxygen atom is associated with a sodium or hydrogen atom, or it may be linked to another silica tetrahedron. The silica tetrahedra can link to form chains (Figure 2), cyclic and larger polymeric structures.

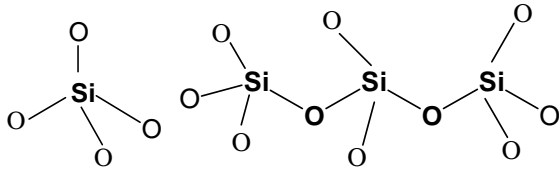
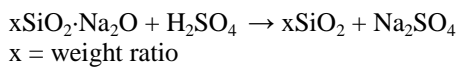


Figure 2: Silicate Monomer, Silicate Trimer.

Regarding sodium silicate, the $\text{SiO}_2:\text{Na}_2\text{O}$ ratio plays a major role in polymerization. The distribution of various polymers is described as speciation and can be affected by concentration and temperature. Below a 0.05 ratio, monomers dominate the distribution. Three-dimensional anions are most abundant in 2.48 and higher ratios. For a 3.22 ratio at increased temperature, the larger cyclic anions are relatively stable, while dimers and monomer increase (PQ, 2004; Iler, 1979; Patterson, 1994). Further additions cause interactions with large silica oligomers and polymers to yield precipitates and gelation. For example, mineral acids will react with sodium silicate as follows:



Another example of this precipitation/gelling phenomenon is the reaction of silicates with polyvalent metal ions to produce metal silicate precipitates that are less soluble across a broader pH range than the metal hydroxides produced by non-silicate processes. Thus, calcium salts react with sodium silicate to form calcium silicate hydrate. This reaction is fundamental in cementing and grouting. The foregoing discussion impacts downhole placement, because the composition ratios will dictate whether a gel or a hard plug is formed.

This ability of calcium salts to form gels and precipitates with metal silicates has been exploited to produce silicate plugs in water shutoff applications. Calcium chloride is a good example of an activator in the formation of stable silicate plugs (PQ, 2004; Iler, 1979).

The work summarized in this paper describes a way of exploiting silicates' unique gelling properties in an environmentally friendly and cost-effective way to form plugs for use in geothermal applications.

Lab Evaluations

Previous studies have shown the potential for using silicates with activators to form plugs for water shutoff (Heaven et al, 1999; Lakatos et al, 2001; Samari et al, 1998; Viddick et al, 1988). New geothermal applications for this technology require the plugs to be able to withstand temperatures of 150° – 300°C.

The screening study was undertaken to assess the potential of several chemicals known to react with N sodium silicate¹ to form plugs and then determine the stability of these plugs at 200°C. Stainless steel bombs were used, which became pressurized at high temperatures. Initial experiments determined whether and how much dilution of the silicate was appropriate to obtain the hardest, most solid plug that retained stability and integrity over time. Table 1 summarizes dilution requirements of the sodium silicate for each activator.

Table 1. Activators & Silicate Dilution Assessments

Activators with N Sodium Silicate without dilution	Activators with Diluted N Sodium Silicate (~ 25% v/v)
Calcium Chloride 10%	Calcium Sulfate – 7.5 % Plaster of Paris Powder
Sulfuric or Nitric Acid 20%	Citric Acid 20%
Hydrochloric Acid 20%	Hydrochloric Acid 50%
Sodium Bicarbonate 10%	Acetic Acid 20%

Table 2 summarizes the initial screening test matrix with the starting materials at room temperature and pressure. All of the activators cause plug material to form in a brief time period, often as quickly as one mixed the solutions. The plug material is of a consistency that can plug holes in rock, and i.e. the material is hard, stiff and cohesive. At room temperature and pressure mixing conditions, it appears that all of these chemical combinations are options. However, additional criteria were invoked to further define the screening. First, the plugs were sealed in a pressure vessel and placed in an oven set at 200°C for 16 hours, then cooled to room temperature and pressure. Some of the plug materials were physically broken down by the heating and cooling process, thus were not tested further. The nitric and sulfuric acids were not tested further because they are not common chemicals at drill sites

¹ The N sodium silicate used in all the experimentation is obtained as a 37.5% solution in water and has a silicate to alkali ($\text{SiO}_2:\text{NaO}_2$) weight ratio of 3.22. In this paper it will be referred to as N sodium silicate or sodium silicate.

and are strong acids, requiring careful handling; the HCl, although a strong acid, is more common at drill sites and was tested further.

Table 2. Initial Screening Test Matrix

Activator	Time to Form Plug	Appearance and Visual Strength Assessment	
		Initial RT	16 Hours at 200°C
Nitric Acid	30 Seconds	Smooth solid plug	Very hard, smooth solid plug with aqueous layer
Sulfuric Acid	30 seconds	Uneven solid plug	Smooth solid plug with aqueous layer
Hydrochloric Acid	45 seconds to 1 minute	Smooth solid plug	Hard, uneven solid plug
Acetic Acid	15 – 30 seconds	Smooth solid plug	Plug breaks down into watery liquid and fine precipitate
Citric Acid	8 – 10 minutes	Smooth solid plug	Plug breaks down into watery liquid and fine precipitate
Calcium Chloride	30 seconds	Uneven solid plug	Hard, uneven solid plug
Calcium Sulfate	2 – 3 minutes (can be longer)	Smooth solid plug	Fine granular mass – easy to press into available space
Sodium Bicarbonate	1 – 2 minutes	Smooth solid plug	Liquid – viscosity increases on cooling but does not reform into plug

The following activators were chosen for further study based on customer interest and availability in the field.

1. Calcium chloride – 10% w/w solution with undiluted N sodium silicate
2. Calcium sulfate – 7% by weight (CaSO₄ is insoluble) with diluted N sodium silicate
3. Hydrochloric acid – 20% w/w solution with undiluted N sodium silicate

All solutions were acclimatized to the testing temperature before mixing.

Effect of Temperature on Plug Formation

For geothermal and steam flood applications, study of plug formation at temperature and pressure is a necessary reality which must be evaluated, as the formation is hot. However, local and transient cooling in a borehole may be realized through

circulation to cool the injection area from ambient temperatures. After plug placement, plug and formation temperatures could again increase. In order to best replicate actual downhole conditions, a step-wise experimental program was developed.

For the beginning of this program, tests were completed in which the sodium silicate and activator were heated in an oven to a specified temperature. The two components were then mixed in the oven and results obtained. Stable plug formation was monitored at temperatures of 25°, 65°, 100° and 150°C (Table 3). (Note: In this lab work we are attempting to observe what happens in a geothermal well. The oven and mixing container are at the stated temperature; the materials mixed were placed in the oven and reached maximum temperatures of boiling when mixed in the oven, while observing the gel time.)

Increasing temperature led to an increase in plug formation time. Once formed, plugs were stable at formation temperature and room temperature.

Table 3. Summary of Bench-Scale Test Matrix

Activator	Gel Time 25°C	Gel Time 65°C	Gel Time 100°C	Gel Time 150°C
CaCl ₂ (10% w/w solution)	≤ 10 s Uneven hard mass	10 – 15 s Hard smooth mass	15 – 30s Hard smooth mass	≥ 30s Hard smooth mass
CaSO ₄ (Solid Plaster of Paris)	3 min. Amorphous mass, can be pressed into shape of container	7 min. Amorphous mass, hardens to a solid granular mass over 12 – 24 hours	12 min. Amorphous mass, hardens to a solid granular mass over 12 – 24 hours	30 min. Initially softer amorphous mass & increased ppt., becomes solid, hard, granular
HCl (20% w/w solution)	≤ 10 s Uneven hard mass	10 – 15 s Hard smooth mass	15 – 30s Hard smooth mass	≥ 30s Hard smooth mass

Long Term Stability Testing

From Table 3, each of the assessments produced materials that we feel should be considered as a plug material at least for short-term plugging needs. We chose to pursue using calcium chloride as an activator, making calcium silicate hydrate as plug material because of cost, ease of use and it is relatively benign.

The next series of tests evaluated the long-term stability of calcium silicate hydrate at elevated temperature and pressure of water. For these tests, samples were placed in a pressure vessel with excess tap water, and heated for times up to 12 weeks and

temperatures up to 300°C. The water pressure resulting from heating the contained water was sometimes measured, but generally the pressures were assumed to be those obtained from the steam tables. The samples were cooled and depressurized weekly, and observed and photographed. No visible changes were observed. All samples, heated at temperatures ranging from 80°C to 300°C and pressures from 14.5 to 1250 PSI, were stable (for example, Figure 3).



3 a. 3 b.
 Figure 3: Calcium silicate hydrate (a) 16 hours at 250 °C, $P_{H_2O} = \sim 680\text{PSI}$ (b) 7 days at 250 °C, $P_{H_2O} = \sim 680\text{PSI}$

Effect of Temperature and Pressure on Plug Formation

As stated above, geothermal and steam flood environments, which are hot and often water laden, motivated sample fabrication in a manner representative of downhole conditions. A set of experiments was designed to simulate at-depth temperature and pressure conditions at the time of the chemical reaction. Because the sodium silicate and calcium chloride have to remain separated (to prevent a reaction), methods were devised to keep the reactants separated until they are exposed to a hot and wet environment.

These methods involve tests with (1) injection of separate component materials into a hot vessel, (2) encapsulation of one of the components, the calcium chloride, and (3) or combinations of injection and encapsulation.

For (1) injection of separate component materials tests, a pressure vessel with a beaker partially full of water is heated. After achieving the test temperature and pressure, the two reactants are separately injected (at a pressure slightly in excess of the internal pressure of the vessel) forming a plug.

For static bulk encapsulation tests, calcium chloride solid was placed at the bottom of a beaker and covered with a layer of wax or thermoplastic to form a permeability barrier. Sodium silicate and water were poured on top of the permeability barrier. The beaker was placed in a pressure vessel and then in an oven already at temperature. At specific

temperatures, the barrier melts and the reaction takes place.

The bulk encapsulation method was refined through encapsulation of individual calcium chloride pellets. The individual pellets can float in N sodium silicate, and will react when heated to a sufficient temperature (at which point the encapsulant melts). (Note: the density of N sodium silicate is 1.39 g/cm³ which can be decreased by dilution with water, and the density of the encapsulated calcium chloride pellets is about 1.3 g/cm³. The process, wherein an encapsulated activator of N sodium silicate is exposed to the silicate through downhole heating allowing a plug-forming reaction to occur, can be extended to downhole geothermal placement (see emplacement scenarios).

Different melting points of the encapsulant enabled observations of the calcium silicate hydrate plug having been formed at different temperatures. Addition of small excess amounts of water to the N sodium silicate did not have detrimental effects on plug formation (some water is in fact needed for a complete reaction). Because calcium chloride is readily soluble in water, when the calcium chloride is exposed through melting of the encapsulant, it dissolves and the calcium reacts with the N sodium silicate. The dissolution of the calcium chloride at room conditions is observed to be exothermic, further facilitating mixing of the reactants in relatively static conditions. This is important because the emplacement scenarios envisioned amount to injecting the two components at the well bottom, thus allowing for the injection and convection of the fluid to effectively cause the mix.

Plug materials formed in this manner were initially studied at two temperature ranges, 80°-90°C and 170°-195°C, the melt temperatures of the encapsulants. However, we extended this experimental program to study the chemical reaction at many temperatures between 90°C and 195°C through injection tests. In the first series of tests, sodium silicate and encapsulated calcium chloride pellets were injected into a hot and pressurized water or water and gravel container. The temperature of the interior of the vessel only has to be equal to or greater than the melt temperature of the encapsulant for the reaction to proceed. When the reactants are injected, they heat up quickly, causing the encapsulant to melt, allowing the calcium chloride to dissolve and then react with the sodium silicate, forming a calcium silicate hydrate solid. Injection testing was further extended to inject into hot and pressurized water-laden gravels with a differential pressure (Figure 4). In this example, formed and kept at relatively low temperature, a stiff gel is observed to form.



Figure 4. Gravel and calcium silicate hydrate agglomerate formed at 90°C.

Adhesion to Rock

The grout must have a finite strength and adhere to rock. No specific mechanical properties tests have been completed on the grout. It is observed that grouts adhere to gravel when the components are mixed in their presence, or when the reactants are injected into hot-wet gravel. When the test system is disassembled, the grout-gravel agglomerate retains cohesion and strength (Figure 4).

Simulated Geothermal Drilling Conditions

Recent tests have focused on injections into gravel while circulating hot water (Figure 5 is a longitudinal section of a completed test, in which the gravel is red and the grout material is white). In these tests an assembly consists of the flow configuration shown (Figure 5) potted in a large thermal mass within an oven set for 120° to 150°C. By flowing a closed loop of water through the assembly, the temperature within the gravel can be maintained at 80° to 90° C. This is meant to simulate the near well bore situation in a geothermal well, wherein drilling fluids are circulated to cool the drill bit and remove cuttings. At a specific time flow is momentarily halted, then the grout reactants are injected, then flow is restarted. Typically no flow is observed, thereby demonstrating the effectiveness of the plug. To further evaluate the plug integrity, the upstream end has been pressurized up to about 300 PSI with little to no flow observed. The results have thus far consistently produced a plug material that adheres to the gravel. The plugging action is observed to clog the pores in the gravel and decrease flow rates by orders of magnitude.



Figure 5. A gravel-packed pipe sample (post test). Arrows indicate water flow and grout injection direction.

Chemical Analyses

A limited number of chemical analyses of samples were completed using X-ray diffraction and Raman Spectra methods, with consistent and sensible results. First, the plug material composition in all samples is calcium silicate hydrate; this composition is consistently found with increasing time at a given temperature of formation. Second, with increasing time and temperature, the crystallinity of the calcium

silicate hydrate increases from amorphous to glass to ordered structures. This appears to indicate the plug will become more stable chemically and mechanically with time (and not degrade under adverse conditions). Also, important to geothermal applications, calcium silicate is acid resistant.

Downhole Placement Considerations

Given the current lack of direct experience with this type of plug in a geothermal environment one can only suggest the following emplacement scenarios for calcium silicate hydrate plugs based on lab and bench-scale testing. In beakers, the plug material is observed to form immediately on mixing. Within a pressure vessel, with only “static mixing” the plug material forms on the bottom, side, and center of the container. In the injection tests the plug material forms when exposed to the hot wet gravel. Consequently, at least two potential emplacement scenarios are envisioned.

Method 1: Upon encountering an extreme loss zone, the drilling could be stopped and the drill-string removed from the hole. The first method is similar to twin streaming. It is unknown at present if a mixing nozzle is required; based on static mixing experiments it appears unlikely. Two hoses would be strapped to the drill pipe and lowered to within 60 ft of the hole bottom. The sodium silicate and activator (calcium chloride 10% w/w solution) would need to be separately prepared in a volume sufficient to fill the bottom 40 ft in preparation for separate pumping from the surface. The two components would be pumped through two separate pipes, and chased with water to help drive the plug a short distance into the formation. We envision that this placement method will allow the plug to travel only a very short distance into the formation, because the mixing and plug solidification will occur in the hole. Filling the hole with water would confirm closure of the loss zone. Twin coil tubing could similarly be used. The use of a drillable tail pipe at the bottom of the drill pipe may be desirable to minimize the potential for cementing the drill pipe in the hole (Figure 6).

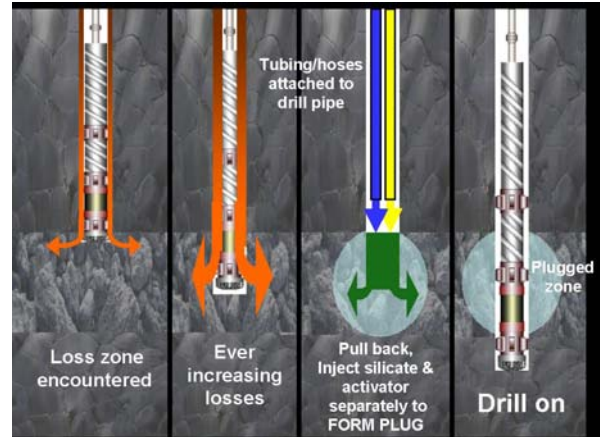


Figure 6. Placement scenario using tubing attached to drill pipe.

Method 2: In the second method, the calcium silicate hydrate plugs would be placed as follows. A measured amount (for the volume determined from the hole diameter and stand-off height) of the mixture for filling the backed off section of hole, with encapsulated CaCl_2 and N sodium silicate could be placed by pumping the constituents down the interior of the drill pipe. The size of coated pellets must be less than 1/3 the drill-bit port diameter. Alternatively if particle size risked bridging the nozzles, the drill pipe could be tripped and runback in open-ended with a drillable tailpipe if deemed necessary. (Note: Some of our encapsulation studies included encapsulation of powders, so encapsulated activator can be quite fine.) The pumping/flow rate would have to be such that all of the plug mix exited the drill bit before melting of the encapsulant occurred. Temperature determinations, coupled with pumping/flow rates would need to be part of this grout system such that the plug forming reaction did not happen inside the drill string. If the downhole conditions had been determined to be excessively hot, perhaps water could be pumped down the drill string for a short time period to cool the drill pipe. The mixture, once delivered, would be heated (by the downhole heat), the encapsulant would melt, and the plug would be formed, sealing the loss zone (Figure 7). It may be necessary to chase this mixture with water (or another fluid) to provide a backpressure to drive the plug a short distance into the formation. It is envisioned that this plug material would flow a short distance into the formation, because the plug-forming reaction is thermally activated. If the drill hole already has water in it, the calcium silicate hydrate plug material will sink to the hole bottom, because it is more dense than water. The drilling could commence in a short time because the plug sets immediately. Each of the methods described should be evaluated through bench-scale and field-testing.

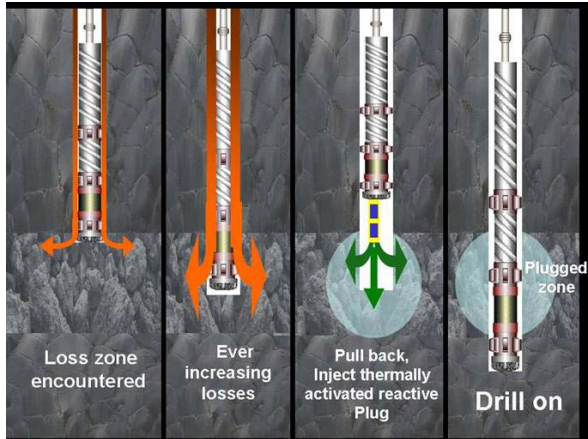


Figure 7. Placement scenario using through drill string delivery system.

DISCUSSION AND CONCLUSIONS

Recognizing the importance of minimizing trouble time caused by severe lost circulation in geothermal wells, water shutoff and steam flooding, we have studied a high temperature grout system that uses silicates. The synthesis and chemical stability of viable high-temperature silicate plugging materials, as well as, placement of the grout material in a hot water laden environment were part of this study. The material complies with the initial needs, namely (1) no special handling requirements and considered non-hazardous by the DOT and EPA; (2) low cost; (3) readily pumpable; (4) controllable gel time; the reaction rate needs to be adjustable for varied conditions both at the surface and down-hole; (5) controllable placement such that it has minimal water solubility and adheres well to rock surfaces through a single delivery hose; (6) hydrothermally stable for 8 weeks at geothermal temperatures (7) once placed, the grout is sufficiently stiff, to drill with conventional means, and no unanticipated problems with drill bit plugging.

Because of their ability to form fast-setting stable gels, we are reintroducing silicates to geothermal applications. There exists the potential to solve high-temperature lost-circulation problems through the use of these fast-setting silicate plugs. The laboratory study has shown that silicate hydrate plugs solidify quickly and maintain their integrity for extended time periods at high temperatures (300°C). In principle, the material should survive at greater temperatures. Encapsulation of one of the plug components allows emplacement at 80°C to 300 °C (and, in principle, at higher temperatures). Simple deployment schemes are presented which may decrease drilling downtime that has resulted from lost circulation.

ACKNOWLEDGEMENTS

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