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Comments on High Temperature Plugs: Progress Report on Polymers and Silicates

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ABSTRACT

Recognizing the importance of minimizing trouble time caused by severe lost circulation in geothermal wells, we have studied the chemical stability of two potential lost circulation plugging materials, polymers and silicates and have integrated each into high temperature grout systems. Both materials satisfy a set of criteria developed to assure compliance development of a high temperature grout system. The polymers developed are pumpable through a single deployment tubular, and are hydrolysis resistant for at least 8 weeks at 350°F. The two components of the silicate hydrate plugging material developed are also believed pumpable through a single deployment tubular, possibly the drill assembly; this is possible because of a novel encapsulation/activation method of one of the components. The silicates are deployable and viable plugs from 150°F to 600°F, for extended times (at least 10-12 weeks). The chemistry and survivability of each of material is discussed as well as potential emplacement scenarios.

Introduction

The following progress report summarizes current laboratory-based advances in developing high temperature plugs for lost circulation zones. The purpose of this research includes developing emplacement systems for and determining the temperature limits of reactive plugs for cross flow. Sandia National Laboratories, through support of the Geothermal Energy Program within 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 150°F to 600°F and 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 typical initial solution to the problem. A typical procedure would be to stop drilling, place the cement plug and allow the cement to cure, then re-drill. However, high cross flow rates and/or large voids 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 cement placed simply may not fill all of the void present.

Through the systems approach taken 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 experienced caused by lost circulation is very costly.

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.

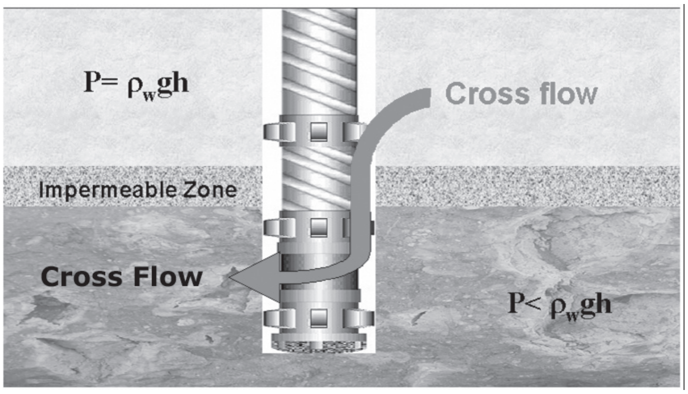


Figure 1. Cross flow occurs when two formations with unbalanced pore pressure (P) and $\rho_w gh$ is weight column of water back to surface.

At Sandia, most of the work to date has focused on polyurethane grout, a preferred reactive plug, based on its material properties and successful deployment at Rye Patch [1]. The primary focus had been to establish the temperature limits of polyurethane grout to determine its suitability for setting a plug in a depleted reservoir. Once emplaced, the grout must be able to survive for up to 8 weeks (the time needed to drill ahead and cement the next casing). In this earlier research, thermally driven hydrolysis of polyurethane grouts was discovered and investigated to determine potential degradation of material properties as a function of time and temperature. The work reported herein has extended previous work in two ways: (1) the polymer compounds have been demonstrated stable from hydrolysis for 8 weeks at 350°F, and (2) the compositions can be mixed at the surface and deployed downhole though a single hose. However, because of the inherent temperature limitations of polymers subjected to hydrolysis conditions (slightly greater than 350°F?), it became prudent to study other materials that potentially could be used as high temperature plugs, i.e. silicates.

Silicates have been used to form stable grouts and cements for over 50 years [2] 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 [3,4,5]. In addition to their gelling action, silicates will also react with soluble metal salts, such as calcium chloride, to produce insoluble metal silicate plugs. Silica is known to be stable and environmentally benign at high temperatures. Because of these qualities, silicate plugs offer great potential for use in geothermal applications. As such, the project evolved into two separate laboratory-based material studies, polymers and silicates.

Polymer Chemistries Studied

The polymer chemistry work reported herein is an outgrowth of previous work at Sandia in conjunction with Green Mountain International Inc [6]. Improving polyurethane grout formulations initially focused upon evaluating the mechanical and chemical integrity of "off the shelf " polyurethane grouts when subjected to elevated temperatures in the presence of water. While cement grouting of casings will continue to be a requirement, cement plugs have proven inadequate to stop lost circulation and cross flows. New reactive plug technologies are needed. Rigid polyurethane was chosen for development as the first reactive plug because of favorable properties including, relative immiscibility in water, fast cure time, low viscosity, and density close to that of water. These properties have made rigid polyurethane the material of choice in civil engineering for sealing boreholes and dams with large voids and high inflows - conditions associated with the worst lost circulation problems.

This work reports on polymer grouts that have been developed to help overcome some of the deficiencies of the cement grouts. Some polymer grouts flash set upon contact activation with water, and when constrained through placement through a packer they will flow (low viscosity) and expand to fill the accessible volume through the nature of the chemical reaction in which they are formed.

In 2001 Green Mountain International, Inc., Sub-Technical, Inc., Resource Group and Sandia National Laboratories joined forces to deploy a polyurethane-based grout to plug a lost circulation zone at Rye Patch, Nevada. Over twenty conventional cement plugs and other common plugging techniques had already been tried on this well without success. A two-part polyurethane grout (Mountain Grout ISP) was used to plug the lost circulation zone and permit completion of the well. The two-part system was chosen because of its availability, shallower depth of 740 ft and low temperature 170°F [1].

The success at Rye Patch inspired a more rigorous laboratory study of polyurethane based grouts. The goals of this work were to include development of a better understanding and improvements upon (1) the deployment technique(s) of polyurethane based grout and (2) the chemical/hydrolysis/thermal stability of polyurethane based grouts. Because lost circulation zones are commonly encountered at much greater depths and higher temperatures than those at Rye Patch, higher survival temperatures are of importance. Also, simplification of the deployment techniques was desired. Therefore, a program to address these issues was initiated.

The desired characteristics of polyurethane based grout systems, in terms of both material development and means of deployment were developed based on the historic Sandia knowledge with the specific field application at Rye Patch. The two-part polyurethane used at Rye Patch was highly reactive and, therefore had to be mixed seconds before dispensing into the lost circulation zone. This problem was resolved by the use of two separate hoses and a static mixer located at the deployment zone. A polymer grout that can be dispensed in the lost circulation zone, as a single component, activated by contact with water, would dramatically reduce the complexity of the equipment needs and broaden the window of reaction time.

The relatively low temperature of the lost circulation zone (170°F) at Rye Patch was compatible with the Mountain Grout ISP. In preparation for other geothermal lost circulation problems the product was tested for hydrothermal stability. The Mountain Grout ISP performed well at temperatures up to 225°F.

A program was initiated to screen a variety of isocyanate reaction products and other polymers in an effort to optimize the hydrothermal performance. The initial needs included development of a material with no special handling requirements and considered non-hazardous by the DOT and EPA. To be competitive with cement, a low-cost alternative is needed because cement is inexpensive. In fact, cement may be often tried many times in a troublesome hole because of its low cost, however associated down time could add up to a significant expense. The polymer must also be readily pumpable, with a 200 cps maximum viscosity at pumping temperature (maximum 100°F surface temperature). We must be able to control the gel time; the reaction rate needs to be adjustable for varied conditions both at the surface and down hole. For example, it must be chemically stable with no pre-gellation at surface or in the delivery hose. We must be able to control the placement such that it has minimal water solubility, adheres well to rock surfaces, and is deliverable through a single hose. Once placed it must be hydrothermally stable for 8 weeks at temperatures exceeding 300°F. Also, once placed, the grout would have to be sufficiently stiff to drill with conventional means, and pose no unanticipated problems with drill bit plugging.

Polyurethane Chemistries Studied, Procedures and Results of Early Testing

This development program involved a sampling of the most promising candidates and evaluated their potential to optimize the hydrothermal performance of the resulting polymer. Isocyanate is the primary building block of conventionally produced polyurethane polymers. Isocyanate can also react to produce other chemical linkages. Some of the reactions and the resulting products included urethane, urea, isocyanurate and cardodimide. The material development and evolution was based on trial and results with specific chemistries during a two-year time span [6]. This extended time duration was long because the hydrolysis testing was designed to determine time-dependent effects.

The original test procedure involved placing small specimens of each sample in a water filled aluminum cup in a Parr Bomb. The specimens were weighted with a metal washer so that they remained submersed in the water. The Parr Bombs were then heated by placing them in an oven and internally pressurized in response to water pressure generated through heating to the desired test temperature. Periodically the specimens would be removed and tested for digestion by manually probing. *Digestion* is the term used to describe the physical/mechanical manifestations of hydrolysis, the chemical process in which water breaks down the polymer bonds. The original lab test procedure used a subjective evaluation; consequently, no definitive time could be assigned for the material's stability. Materials tended to deteriorate gradually by swelling, softening or breaking. Based on the observations recorded for these tests, conclusions were reached [6] which were used to guide further research and development work.

Additional samples were prepared to re-evaluate some of the materials along with some refinements indicated by early results. These samples were prepared with greater effort to produce specimens of more consistent proportions and densities. The evaluation procedure was also modified to provide more objective comparisons (described below). The final series of materials prepared for testing included samples that were: water activated, water and heat activated, heat activated polyurea, and heat activated polybutadiene resin and dimethacrylate monomer.

As part of establishing the test procedure, tests were done at elevated pressures (pressures in excess of the vapor pressure of water) and also with insufficient water such that all the water evaporated. A slight increase in the degradation rate was observed as the pressure was increased to ~1,500 psi, but this increase was on the same order as variability from sample to sample. This increase was attributed to the increased rate that water diffused into the samples at elevated pressures. At pressures below the vapor pressure of water (no liquid phase present) degradation was minimal. This requirement of a liquid phase for hydrolysis of the polyurethane was interpreted as the explanation for why many materials claiming to be stable at elevated pressures, do not perform well downhole – they have temperature rated based on thermal degradation in air by oxygen attack, rather than in water due to H^+ and OH^- attack.

For the final series of tests, the evaluation procedure was supplemented to include durometer readings thus improving the objectivity of the testing. This quasi-quantification of the mechanical integrity of final polyurethane grout compositions utilized the standard test method for rubber property, durometer hardness (ASTM 2240). Thus, the method allowed us to provide a valid comparative measure of changes in mechanical integrity of polyurethane resulting from hydrolysis. Other tests were tried (gas chromotography, dynamic modulus, and thermal gravimetric), but were found less repeatable than the durometer.

Samples were evaluated for hydrolytic stability by placing small wedge shaped sections of each into the test bomb at 275°F and ~45 PSI; 300°F and ~67 PSI; 325°F and ~96 PSI; and 350°F and ~135 PSI. At regular time intervals, the vessel was removed from the oven, cooled, and durometer readings were taken and plotted. A 50 % drop in durometer reading was arbitrarily chosen as the "end point" to obtain days of stability at the test conditions and thereby rank the materials. The best performing materials at 275°F were selected for 300°F testing. The best performing materials at 300°F were selected for 325°F and then 350°F testing; both survived 56 days.

Discussion of Polyurethane

The evaluations are based on single specimens representing each formulation variable. While a 50 % decrease in durometer hardness was chosen as the "end point" for comparative purposes, since the initial durometer readings varied, a specific durometer requirement may offer a more accurate assessment of performance capability.

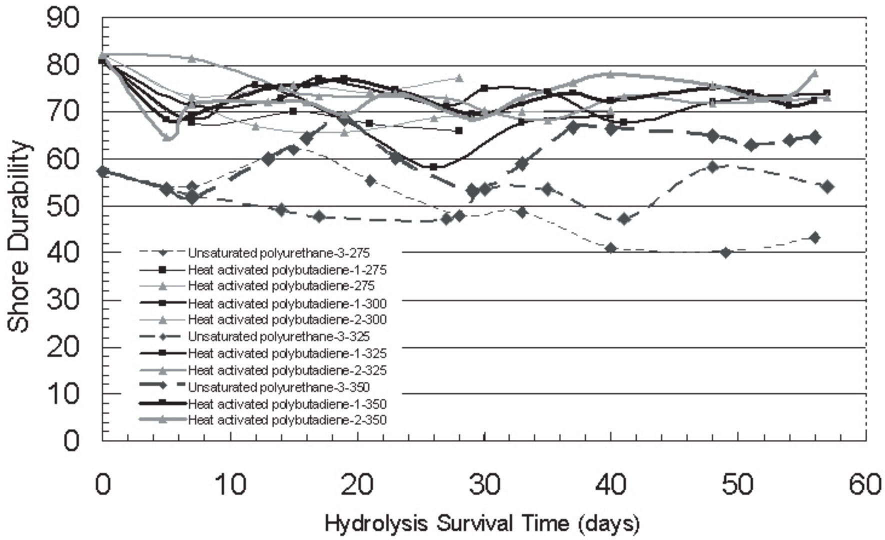


Figure 2. Shore durability vs. hydrolysis survival time.

Earlier results had suggested that more urea linkages from the isocyanate-water reaction would improve hydrothermal performance. DEG-2-35-2 failed to demonstrate this enhanced performance. (We used a systematic test material identification system that consisted of **DEG-A-B-C**. **DEG** stood for Dennis E. Galbreath, chemical fabricator. **A-B** represented a chemical family, and **C** represented variations on the **A-B** chemistry.)

Polybutadiene is very hydrophobic and (DEG-2-36-1) was expected to offer improved performance over the standard polyether polyol (DEG-2-35-1). The test results did not agree with this expectation. This performance confirms that of earlier test results.

Based on the test results of formulations containing significant urethane linkages, the failure of this linkage appears to limit its usefulness to temperatures up to 275°F. No substantial difference in performance was observed between polyols based on propylene oxide or ethylene oxide. Polyols with greater functionality should enhance performance slightly but were not used due to the higher viscosity of the resulting prepolymers. High viscosities make it difficult to pump the material.

When additional crosslinking was introduced through the use of dimethacrylate monomer and the polybutadiene, substantial improvement was observed as demonstrated in samples DEG-2-36-2, DEG-2-36-3, DEG-2-38-1 and DEG-2-38-2.

The production of polyurea linkages from the reaction of isocyanate and amine appears to be more stable than those produced from the reaction of isocyanate and water. This may be due to incomplete conversion due to stearic hindrance when trying to react the tightly compacted aromatic isocyanate molecules that must first react with water to create an amine that then must react with another isocyanate molecule to form the substituted urea.

The increase in the isocyanate to amine ratio with the DEG-2-37 series from 1.0 to 1.2 to 1.4 failed to improve the hydrothermal performance. DEG-2-37-1 demonstrated good performance while DEG-2-37-2 & 3 showed a progressive decline in performance suggesting a chain terminating effect or susceptibility of the biuret linkage to hydrolysis.

The elimination of isocyanate reaction products (DEG-2-38-1 & 2- [both heat activated polybutadiene]) helps to demonstrate that those linkages are limiting the hydrothermal stability of the polymers. Ultimately these latter compositions were judged to have survived the best (along with DEG-36-3-unsaturated polyurethane).

The Shore durability test results are shown in Figure 2 as a means to demonstrate a summary of the mechanical integrity and its changes with time of the best of the polymers studied through 350°F. Materials represented all survived hydrolysis, that is they all retained >50% of their initial Shore durability. Our judgment is that there is no apparent effect of hydrolysis for any of these samples (Figure 2).

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°F to 600°F. From the initial screening, calcium chloride activated plugs were chosen for further testing and were found to be stable for long periods of time at high temperatures. No other activators, carriers or cross-linking additives were required for the successful formation of high temperature stable, impervious, solid silicate plugs.

Water shutoff and lost circulation [2,3,4,5] 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 [2,3,4,5]. This stability is carried through to the plugs formed with calcium chloride.

The work summarized in this paper describes a novel way of exploiting silicates' unique gelling properties in an environmentally friendly and cost-effective way to form plugs for use in geothermal applications. 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 tetrahedral silicon atom at the centre of an oxygen-cornered, four-sided pyramid (Figure 3). Furthermore, each oxygen atom may be associated with a hydrogen or sodium atom, or it may be linked to other silica tetrahedra. At higher ratios the oxygen may be linked through tetrahedral co-ordination (Figure 4).

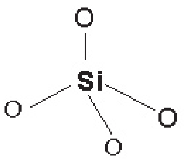


Figure 3. Silicate Monomer.

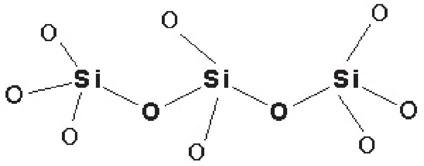


Figure 4. Silicate Trimer.

The SiO_2:Na_2O 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, monomer dominates the distribution. Three-dimensional anions are most abundant in 2.48 and higher ratios. For a 3.2 ratio at increased temperature, the larger cyclic anions are relatively stable, while dimers and monomer increase [7]. Excessive additive concentration can interact with large oligomers and polymers in silicates to yield precipitates and gelation. An example of this phenomenon is the reaction of calcium salts with silicates to form calcium silicate hydrate, C-S-H. This reaction is fundamental in cementing and grouting.

The above discussion impacts downhole placement, because from the above, the composition ratios will dictate whether a gel or a hard plug is formed.

The 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 silicate plugs [5,7].

Lab Evaluations

New geothermal applications for this technology require the plugs to be able to withstand temperatures of 300°-600°F in wet, potentially briny environments. An equally important requirement is formation time, it must be in the seconds to minute's time frame in order to arrest a severe loss zone or cross flow.

A short screening study was undertaken to assess the potential of several chemicals, or activators, known to react with sodium silicate to form plugs and then determine the stability of these plugs at 400°F. These activators included calcium salts, mineral acids and organic acids [7]. The plugs were produced at room temperature and monitored for stability at temperatures above 400°F. The most stable plugs were those formed with mineral acids and calcium salts as activators.

Following this original screening, further studies were conducted on plugs formed with N® sodium silicate and calcium chloride. (N® sodium silicate solution is a trade name of PQ Corporation for a 3.22 weight ratio sodium silicate, 37.5% solution in water.) Once formed, the plugs were monitored for stability.

N® sodium silicate was used in all the experimentation. This silicate is obtained as a 37.5% solution in water and has a silicate to alkali (SiO_2:NaO_2) weight ratio of 3.22. Calcium chloride was used in both solid and 10% w/w solution.

1. Screening experiments: N® sodium silicate and various activators were mixed in appropriate amounts to produce a plug at room temperature. The silicate/activator mix was stirred vigorously until a gel began to form and then left to stand until the gel formed a solid plug.
2. The plugs were then subjected to a temperature of 400°F overnight and inspected for stability of shape, hardness and syneresis.
3. A new series of plugs was then prepared with calcium chloride at temperatures of 25°, 80°, 150°, 200°, 300° and 400°F and monitored as above. (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.)
4. Plugs were also studied for stability over time and temperature.

All the activators were chosen based on their use in commercial applications such as silica gel production and water treatment [7]. In all cases the activator was added to N® sodium silicate with vigorous mixing until a gel began to form. Commercially produced silica gels are formed in this way [9].

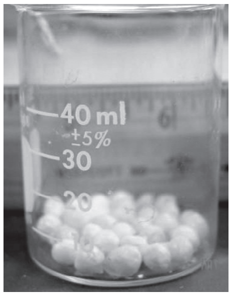
The combination of calcium ion and N® sodium silicate to form calcium silicate hydrate is termed a C-S-H plug. Calcium silicate hydrates are structurally complex and can range from semi-crystalline to amorphous phases, thus resembling natural minerals. Calcium chloride was chosen for further testing as a C-S-H plug activator. This was based on ease of plug formation and stability at 400°F.

With the increase in plug formation temperature, there was no aqueous layer and no syneresis. The plugs were very hard and impervious. It is known in the commercial preparation of silica gels that hydrothermal treatment leads to a loss in surface area and strengthens the gel against shrinkage during drying [8].

Parallel to the tests described above, a second set of experiments utilized small pressure vessels placed in an oven to make the plugs. These tests added the variable of water pressure to the experiment test condition. Because the N® sodium silicate and calcium chloride have to remain separated (to prevent a reaction), methods were devised to encapsulate the calcium chloride. Another reason to separate the materials was to study reactions **at** temperature (i.e. in a geothermal environments, the plug material(s) will be injected into a hot environment). The calcium chloride was first separated from the N® sodium silicate by using a layer of wax or thermoplastic to form a physical barrier in a reaction container (bulk encapsulation). At specific temperatures, the barrier melts and the reaction takes place. Different melting points of the encapsulant enabled observations of the C-S-H plug having been made at different temperatures. Addition of 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 quite soluble in water, when the calcium chloride was 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, and allowing for the injection and convection of the fluid to effectively cause the mix.

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 specific gravity of density of N® sodium silicate is 1.39 g/cm^3 [can be decreased by dilution with water], and the density of the encapsulated calcium chloride pellets about 1.3 g/cm^3 [can be modified]. The process, wherein an encapsulated activator of N® sodium silicate is exposed to the silicate through downhole heating, thus allowing a reaction to occur and forming a plug is felt can be extended to downhole geothermal placement (see emplacement scenarios).

In early work, dried pellets of $CaCl_2$ were encapsulated in liquid thermoplastic or wax and then the coated pellets were plucked from the encapsulant and dropped in ice water. This freezes and sets the thermoplastic, having coated the $CaCl_2$ pellets (Figure 5a). The coated pellets can then be placed in N® sodium silicate with (or without) additional water and no reaction occurs, in fact the coated pellets are observed to float in the N-sodium silicate (Figure 5b). One can wash away bits of uncoated $CaCl_2$ with water, as it is readily dissolved. (Note: a small amount of uncoated $CaCl_2$ does not have a detrimental effect on this process.) During this test, we placed the beaker in a small sealed pressure vessel, in the presence of water, in an oven preheated to 325°F. The sample shown in Figure 5c was removed from the oven after 16 hours. The plug material adheres to the beaker wall, and the beaker must be destroyed to remove the plug material. (Note: Additional means to encapsulate the $CaCl_2$ were studied, for example, powdered $CaCl_2$ can be mixed thoroughly with molten encapsulant, solidified, ground up, and washed [with water] of excess $CaCl_2$. This process broadens the encapsulant particle size range.)


5a.


5b.


5c.

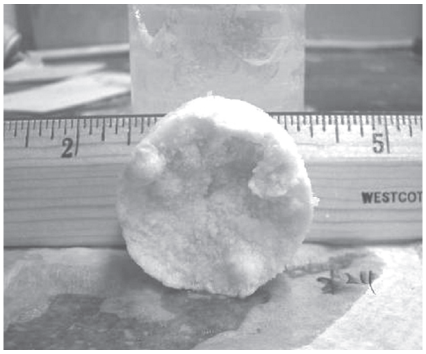
Figure 5a. $CaCl_2$ pellets encapsulated in thermoplastic.
Figure 5b. Unreacted $CaCl_2$ pellets encapsulated in thermoplastic, floating in N® sodium silicate and water (room temperature).
Figure 5c. Ca-silicate hydrate plug formed at 325°F. The thermoplastic was removed for the photo. The red arrows outline the plug.

The exact reaction time for these plugs to form was unknown. However, the solid plug formed in the time it took for the interior of the vessel to heat to the ambient oven temperature (varied from 200°F to 600°F), by monitoring internal vessel temperature (1 to 2 hours). Once formed, the calcium chloride activated silicate plugs were stable at the same temperature used in their formation. Figure 6 shows the same plug material for short and extended times and Figure 7a for at least 12 weeks. This was determined by subjecting a sample to high temperature (400°F and ambient water pressure in the sealed pressure vessel). (Note: Preliminary work has been completed in which encapsulated calcium chloride and N® sodium silicate has been injected into hot (150-400°F) pressurized water. A solid plug is observed to form in seconds, Figure 7b.)

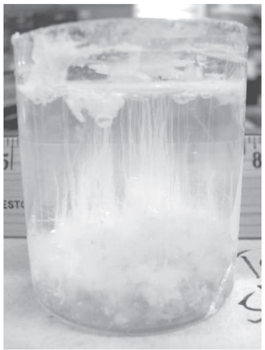
(a) 16 hours at 482°F, P_{H2O}= ~680psi

(b) 7 days at 482°F, P_{H2O}= ~680psi

Figure 6: Calcium silicate hydrate.



(a)



(b)

Figure 7a. Calcium Silicate Hydrate plug, 12 weeks at 392°F, P_p=~225 psi.
Figure 7b. Calcium Silicate Hydrate plug material formed by injection of $CaCl_2$ TEA and N® sodium silicate into pressurized water at ~300°F.

The high temperature plug/grout system described here is described as thermally encapsulated/activated [TEA] silicate plugs. The activator (here calcium chloride) is encapsulated by submerging it in a melted material that is solid and impermeable at room conditions and that will later melt down hole, to release the activator. Once released, the activator dissolves in the presence of free water, and reacts with the N® sodium silicate to cause the hydrate to precipitate. Initial work has used thermoplastics and waxes as encapsulants. Some preliminary work with gelatins has also been attempted. Waxes can be tailored to melt over a range of temperatures (140°-175°F) and the thermoplastic used in this study melts and flows at about 300°F. We have had success in experimentally isolating the activator from the N® sodium silicate, and thus delaying the reaction until a certain temperature is reached. The melting points of both thermoplastics and paraffin can be adjusted through compositional changes. This understanding may be important for different downhole delivery situations.

Polymer Emplacement Scenario Method

Polymer placement in a geothermal well has been successfully demonstrated [1]. Here, we summarize this method with slight modifications resulting from this work (the new chemistries dictate minor, but beneficial changes to the procedure).

DEG-2-38-1 and DEG-2-38-2 are unsaturated polymers that cure by free radical polymerization of those double bonds. The polymerization can be catalyzed by a variety of peroxides. The activation temperature (150o– 250oF) can be changed with the selection of the peroxide catalyst. The activation temperature would have to be chosen based on downhole measurements, and the peroxide catalyst added. If cooling of the hole was needed, this could be done through the drill string.

1- Start with a clean hole, and then temperature, pressure, and caliper log the interval to pick the packer set point. If appropriate supplement these logs with a video log, adding fluid to watch flow and pick packer set point >4ft above loss zone. Determine fluid level to set check valves and determine packer inflation pressure.

2- Backfill to 4 ft below loss zone to control placement and minimize polymer required.

3- Make-up polymer assembly placing bladed centralizer above last drill pipe joint.

4- Run-in-hole while banding hose, pressure gage cable, and capillary tubing to drill pipe.

5- Inflate packer to required pressure controlling pressure with regulator.

6- Add fluid to annulus to test effectiveness of the packer seal.

7- Pump polymer grout at predefined rate watching for leakage past packer.

8- Fill hole to test plug. Drill out hole. Log interval. Repeat polymer job if necessary.

Silicates Emplacement Scenario Methods

Currently, with lack of direct experience with this type of plug in a geothermal environment one can only suggest the following emplacement scenarios for C-S-H plugs. In beakers, the plug material is observed to form as quickly as one can mix. Within a pressure vessel, with only "static mixing" the plug material forms on the bottom, side and center of the container. Two emplacement scenarios are envisioned thus far which appear less complicated and time consuming than that used for polymers.

Upon encountering an extreme loss zone, the drilling could be stopped and drill string removed.

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 is unlikely. Two hoses would be strapped to the drill pipe and lowered within 60 ft of the hole bottom. The N® sodium silicate and activator (one of the species described above appropriately diluted, e.g. mineral acids or calcium salts) would need to be separately prepared in a volume sufficient to fill the hole bottom 40 ft in preparation for separate pumping from the surface. The two components would be pumped, and chased with water to help drive the plug a short distance into the formation. If the pumping and flow down hole did not provide sufficient mixing to form a plug, a mixing nozzle could be added. 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.

In the second method, the TEA C-S-H plugs would be placed as follows. A measured amount (for the volume determined from the hole diameter and stand off height) of the mixture, to fill the backed off section of hole, of encapsulated $CaCl_2$ and N® sodium silicate could be pumped 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 TEA can be made to 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. If the downhole conditions had been determined excessively hot, perhaps water could be flowed 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. 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. If the drill hole already has water in it, the C-S-H plug material will sink to the hole bottom, because it is denser than water. The drilling could commence in a short time because the plug sets in a very short time. Each of the methods described should be evaluated through bench scale and field-testing.

Discussion and Conclusions

Recognizing the importance of minimizing trouble time caused by severe lost circulation in geothermal wells, we have studied the chemical stability of two potentially viable plugging materials, polymers and silicates. Both materials comply with the initial needs, (1) no special handling requirements and considered non-hazardous by the DOT and EPA; (2) a 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 would have to be sufficiently stiff, to drill with conventional means, and no unanticipated problems with drill bit plugging.

Early in the study, it was found the polymers, polyurethane in particular, were susceptible to hydrolysis, wherein water molecules attacked chemical bonds, breaking them through time, and reducing the mechanical integrity of the polymers. This rendered the polymers useless in the desired range of geothermal temperatures and pressure applications. Through a systematic approach many potential chemical variations of polyurethane were developed which tolerated hydrolysis for

8 weeks at 350°F. Secondly, these polymers could be mixed at the surface, and delivered though a single hose or tubular downhole, simplifying deployment.

Specifically, for maximum hydrothermal performance the crosslink density, types of crosslinks and the ability to perform these curing reactions under the field conditions are critical to the ultimate performance of the grouting system. The selection of commercially available and competitively priced raw materials suggest that the standard polyurethane prepolymer and the variations tested will offer about two weeks of useful life at 275°F. The production of aromatic polyureas or polyurethanes crosslinked with dimethacrylate monomers increases the useful life at 275°F to four to eight weeks. By incorporating a polybutadiene resin and crosslinking with dimethacrylate monomer the useful life at 275°F is over eight weeks. By eliminating all isocyanate reaction products and crosslinking a polybutadiene resin with dimethacrylate monomer, the useful life at 300°F is further extended. Testing of final compositions at 325°F, 350°F demonstrated survival from hydrolysis for eight weeks. The two new polymer grouting systems have yet to be tested in a field-type application.

Secondly, we are reintroducing silicates to geothermal applications as a material with the potential to be used to solve high temperature lost circulation problems by their ability to form a fast setting plug. The laboratory study has shown the silicate hydrate plugs to solidify quickly and maintain their integrity for extended time periods and high temperatures (600°F). In principle, the material should survive at greater temperatures. A novel means to encapsulate one of the plug components was developed, enabling emplacement at 150°F to 600˚F. Simple deployment schemes are presented which may decrease drilling down time which has resulted from lost circulation.

Lost circulation is an ever-present problem in geothermal environments. These two materials and methods represent new tools to address this problem. A greater survival temperature for the polymers has been demonstrated, as well as greater temperature maximums represented by the silicates. The costs of silicates is low, the set time is seconds to minutes; these coupled with the through-drill-stem-deployment will decrease trouble time (and costs) from lost circulation. The method allows for decreased delays in responding to and remediation of lost circulation in a high temperature environment.

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