USING CRYSTALLIZED SUPERABSORBENT COPOLYMER FOR PLUGGING HIGH-PERMEABILITY CHANNELING AND VUGULAR COMMUNICATION

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ABSTRACT

As fluids are produced from a reservoir, zones of higher permeability and correspondingly higher flow rates create channels for the preferential movement of fluids. This can result in diminished sweep efficiency when there is premature communication between an injector and a producer.[1] Crystallized superabsorbent copolymer (CSC) is a water-swellable (but not water-soluble), 100% crystalline synthetic polymer. CSCs are resistant to degradation by CO_2 and bacteria and have a temperature range of 70° to 275°F. In addition, rigless placements can be made down current injection tubulars, eliminating the expense of using a workover unit.[2]

This paper addresses the uses of CSC in the Permian Basin for the treatment of vugular communication, lost circulation, and near-wellbore remediation problems.

INTRODUCTION

The formations discussed in this paper include the Grayburg, San Andres, Glorieta, and Paddock. Geologically, all are formations of the Permian Age. The Permian strata was deposited ~250 to 300 million years ago and is the last period of the Paleozoic Era (roughly 250 to 542 million years ago). It is further subdivided into six geologic periods. From oldest to youngest these geologic periods are: the Cambrian, Ordovician, Silurian, and Devonian. These formations were deposited in shallow-shelf carbonate environments along the western shoulder of the Central Basin in west Texas and SE New Mexico. Natural fractures and karsted intervals typically dominate the injection paths and can be very directional. Variations in the content of anhydrite within these dolomite formations contribute to the large differences in the geological stress and integrity of the intervals. There are significant permeability variations ("fast tracks") causing the majority of the injected fluid to sweep only a small percentage of the zone.[1,3]

In addition to the variations in permeability and porosity, the formations are layered and the anhydrite composition varies from a small percentage to the dominant rock content. Chemically, anhydrite is calcium sulfate. It is not formed directly, but is the result of the dewatering of the rock and is commonly referred to as the mineral gypsum. This dewatering results in a reduction in volume of the rock itself. Hence the presence of large voids and caverns in this type of formation are not uncommon.

These formations are characterized by multiple layers with discontinuous areas caused by widespread impermeable layers. Today, most of the recovery in the Permian Basin is achieved via pressure maintenance using water flooding and miscible floods using CO_2. Permeability contrasts within the various layers are responsible for the varying degrees of effectiveness of water and CO_2 injections. Development has led to many injectors communicating directly to the offset producers. This usually becomes more evident when CO_2 operations begin. Typical completion depths are 3,000 to 6,500 ft.

Conditions in lithology, rock structure, and geological histories can limit the ability to achieve a balanced flood due to the rock properties and architecture existing in the reservoirs. Fractures, fissures, and highly eroded permeability may exist due to these naturally occurring conditions or can be caused by operational practices and old completion methods.[4]

DESCRIPTION OF PROBLEM

Wellbore losses and lack of integrity usually display similar conditions with a potential for water influxes and cross-flows prevalent within the problem intervals. Often, injectivity patterns follow fracture paths that lead across flood units and offer dynamic interference to any attempted solutions meant to remedy the conditions. Hazardous conditions also exist with the presence of H_2S and iron sulfide content.

A method to modify the injection flow paths in wells containing fissures and/or a fracture network is desired. This type of modification is one of the most difficult problems to solve because of the vast amount of vugular fill required. Ideally, by squeezing off injection into the voids associated with the "fast tracks" in the injection zones, subsequent injection will be directed into previously "unswept" portions of the interval. The goal is to be able to increase treatment success and the accompanying economic benefits by reducing waste and inefficiencies resulting from the out-of-zone injection.

PAST APPROACHES

With the apparent dynamics of fracture systems and interpretation from historical water-flooding records, indications of possibly eroded and leached-out fracture systems have traditionally been treated with foamed cement. This has met with limited success. A dynamic, energized sealant system, such as foamed cement, is usually needed to stop the losses in injection and interwell communications within the highly communicated fractured interval(s). In addition to foamed cement, other solutions have been attempted:[5,6]

1. Liquid systems with in-situ polymerization post-placement.
2. Fibrous materials that produce a flexible blockage.
3. Reactive chemicals with both internal and external catalysis.
4. High-strength, highly efficient displacement materials capable of blocking or modifying fracture systems with rapid communication between wellpairings.

CSC PROCESS

The CSC process involves a dehydrated crystal consisting of a swellable, crosslinked network of polymers. The CSC particles swell by absorbing 40 to 400 times their weight in water. They are made from crosslinked polyelectrolytes (i.e., polymers with charged pendant groups). Typically, they are either copolymers of acrylamide and acrylate monomers, or homopolymers of acrylate crosslinked by traditional methods. Another type is made of biodegradable starch backbone grafted with acrylonitrile and acrylate.

CSC particles are available in sizes that range from 1 mm to 14 mm, with options for smaller grind upon request. This unique technology offers the ability for these discrete particles to enter fissures and/or fracture systems without intrusion into the matrix of the rock.

Sufficient volume of the CSC is pumped to positively influence the injection flow path through the fracture system. One method to determine the volume required is accomplished by use of an injectivity analysis or a "step rate" technique.

Once the CSC is pumped into the fractured interval, the well is shut in for a period of ~3 hours to allow the CSC particulates to hydrate and swell. Laboratory evaluation has proven that the CSC will increase in size from 100 to 400 times its original volume when exposed to fresh water and up to 25 to 50 times in brine production water.

CSC treatments using produced water generally result in a swelling time of approximately 45 minutes. The swelling time may be decreased to as little as 20 minutes by using fresh water to place the material. Ideally, placement of the CSC should reflect an increase in pressure, which is an indication that the fracture system has received a sufficient treatment volume to achieve diversion. The volume of the treatment is basically by trial-and-error design as the capacity of the fracture, void, or fissure is being filled. A suggested flow diagram is shown in **Figure 1**.

EVALUATION PROCEDURE AND RESULTS[7]

The swelling factor, SF (w/w), of the CSC materials was evaluated at different conditions as a function of time. The following procedure was used:

1. Multiple 4-oz. bottles were filled with 100 gm of the carrier fluid. The number of bottles depended on the desired number of data points for a particular test.

2. A specific water-swellable material was added to the carrier fluid, keeping the same concentration (w/w) in each bottle.
3. Solutions were mixed with a stir magnet for 2 minutes.
4. Bottles were sealed and placed in a water bath at testing temperature (i.e., 135°F). This stage of the experiment was considered to be time 0.
5. After 5 minutes, one of the bottles was taken out of the water bath and the contents underwent vacuum filtration (using a Buchner funnel, filtering flask, filter paper No. 2, and 20 to 25-in Hg vacuum).
6. The amount of water left after filtration was measured to determine the amount of water absorbed by the granulated water-swellable material. The swelling factor was equivalent to the number of times the granulated water-swellable material increased its original weight as given by:

$$SF_{t=t_1} = \frac{\left(w_{carrier\ fluid,t=0}\right) - \left(w_{carrier\ fluid,t=t_1}\right)}{w_{swelling\ material,t=0}} \qquad \textit{Equation 1}$$

where:
SF = Swelling factor
w = Weight in grams (g) of either the carrier fluid or water-swelling materials at a given time
t = Time in minutes (min) after the materials were immersed in water

The same procedure was repeated for each bottle at different times.

Example: The test began with 100 g of 1% NaCl solution and 3 g of the CSC at designated time zero. After 60 min, 72 g of solution were extracted, which indicated that the CSC had absorbed 28 g of 1% NaCl solution. The swelling factor was calculated as follows:

SF = (100 g – 72 g) / 3 g
SF = 9.3

In this example, the CSC increased in weight 9.3 times (SF) after being immersed for 60 min in 1% NaCl solution.

Figures 2 through 4 summarize the CSC's swelling properties under various conditions. Most of the testing was performed with the 4-mm particle size. As expected, the CSC showed the highest SF (w/w) in fresh water. High-salinity fluids lowered the SF significantly. $CaCl_2$ water slowed down the swelling rate of the CSC drastically, and no swelling was observed in kerosene. Higher temperatures seem to slightly increase the SF as illustrated in Figure 4. Figure 2 shows that the smaller the particle size, the faster the swelling due to a greater surface area contacting water.

EXTRUSION CORE-FLOW TEST

The ability of the CSC to withstand high differential pressures was evaluated using an impermeable synthetic core with a simulated fracture that ran throughout the length of the core (**Figure 5**). The core was created to be impermeable so that the only path of the fluid injected into the core would be through the fracture.

The CSC was packed manually into the fracture of the core. Two 100-mesh screens were placed at both ends of the core. The carrier fluid was flowed through the core and the differential pressure was monitored as the swelling CSC was filling the fracture (test was performed at 135°F). As **Figure 6** illustrates, it took approximately 10 minutes for the CSC to swell and fill the capacity of the fracture, increasing the differential pressure from > 1 psi to 1,000 psi. The CSC completely shut off the flow of water through the fracture (differential pressure was limited to 1,000 psi). The test was then shut in and evaluated every other day for three weeks as shown in **Figure 7**. In addition, testing temperature was increased from 135 to 275°F after one week to evaluate the thermal stability of the CSC system at this temperature.

LONG-TERM THERMAL STABILITY IN H_2S AND CO_2 ENVIRONMENTS

The stability of the water-swelling materials under H_2S and CO_2 were visually evaluated under the conditions listed below.

- 165,000 ppm TDS brine water
- 7.5% H_2S
- 1.2% CO_2
- 135°F

The evaluated preswollen CSC was placed in 165,000-ppm TDS brine water in separate 40-mL glass vials. Each water-swelling material was mixed at 2% concentration. Glass vials containing samples were placed without lids inside the test cell (**Figure 8**). All valves were closed. Gases were injected in the following order: CO_2 (1.2%), H_2S (7.5%), and N_2 (91.3%). The temperature was raised to 135°F and the cell was shut in. The cell was depressurized once weekly for observation, and pressured again to continue exposure to contamination up to one month.

Figure 9 shows the results of the visual degradation tests for the CSC material. The first photo shows the control test, while the last photo shows the sample after H_2S and CO_2 exposure for one month. No visual degradation was observed after 30 days of exposure to 1.2% H_2S and 7.5% CO_2 at 135°F in 65,000-ppm TDS brine water.

CSC PLACEMENT TECHNIQUES AND CONSIDERATIONS

1. Establish injectivity into the well at a rate determined from the injection survey. Inject a preflush of 10 bbl fresh water or produced water based on swelling-rate requirements determined for the candidate well.
2. Add the CSC "on the fly" while injecting the desired ratio (fresh water, produced water, designer brine, etc.) into the injectant.
3. Squeeze to the desired maximum pressure to block off the current fracture systems and not fracture the other portions of the injected or produced reservoir.

Note: It is also desired to leave a barrier in the fracture system directionally toward most offset producer(s). If the maximum pressure is achieved during the CSC injection, stop injection and shut in the well. It would be necessary to perform a cleanout via coiled tubing with considerations of acidizing the open hole to gain injectivity and removal of damage.

CSCs can be pumped "on the fly" with a rigless setup. A continuous level additive mixing (CLAM) tub and an injector (**Figure 10**) with a metering system is sufficient to pump the CSCs.

The injector (**Figure 11**) is needed to control the rate at which the CSCs will be pumped. The rate can be controlled manually by adjusting the width of the injection point (**Figure 12**).

A typical treatment may consist of varying the size of the CSCs in addition to varying the concentration of each of the sizes. For example, an operator may want to begin the treatment with 0.5 lb/gal of 1-mm CSC and ramp up to 2 lb/gal of 4-mm CSC allowing the smaller vugular areas to be blocked off first. Other treatments may consist of pumping one-size crystal at a set rate throughout the entire job.

CASE HISTORY

An openhole completed lateral CO_2 WAG injection well in the San Andres formation had not performed as desired in developing a sweep of upper-structure pay and indications were that an injection-profile problem existed. It was ascertained that all injection fluids were entering into a known 30- to 40-ft interval approximately 230 ft from the toe of this 1,337-ft horizontal lateral, rendering the remaining lateral section ineffective. Tracer surveys and interference pressure tests showed most injection fluids were being lost from the productive interval and not giving the desired response to offset producers. A conformance design using a dehydrated crystallized copolymer was implemented to control the loss of injection fluids into the unwanted zone. With confirmation of a positive treatment response, a coiled-tubing stimulation utilizing 135°F heated acid was performed to improve injectivity into the desired intervals within the remaining lateral section.

Post-treatment injectivity pressure response indicated the dehydrated crystallized copolymer conformance treatment successfully sealed off the unwanted injection zone. The followup stimulation was successfully executed. Prior to treatment, it was estimated that 80% of the initial 3,000-mcfd CO_2 injection was being lost into nonproductive zones or communicating directly with a nearby producer. Improved withdrawal rates of 48% from surrounding producing wells following the treatment also suggest that the dehydrated crystallized copolymer squeeze treatment along with the followup coiled-tubing heated acid stimulation was an effective technique to address the poor well performance.

The operator's 30-day payout on the treatment exceeded expectations and set a new conformance standard. Nine months post-treatment, offset production increases in excess of 63 BOPD were observed. CO_2 injection in Well 7C-11H was reduced to one-half the original rate at the same injection pressure of 1,135 psi. Current production in offset wells indicates continued improvement.[8]

CONCLUSIONS

- The CSC was successfully evaluated and considered capable of shutting off fractures and vugular zones.
- CSC is capable of absorbing up to 400 times its own weight in water in a matter of hours. Swelling rate can be slowed by increasing the salinity of the carrier fluid, particularly using $CaCl_2$ brines.
- CSC swelling can be observed within 20–30 min during the core-flow experiments when pressure starts increasing as the carrier fluid is injected into the core and the prepacked CSC begins swelling inside the simulated fracture.
- Based on the vial and core-flow tests, the three evaluated materials do not degrade in the presence of 1.2% H_2S and 7.5% CO_2 at 135°F in 165,000-ppm TDS brine water. The CSC material therefore proved resistant to simulated H_2S and CO_2 environments.
- CSC is already a commercial product available in five particle sizes (approximately 170 jobs have been performed using this material).
- CSC effectively withstood up to 1,000-psi differential pressure in a core-flow experiment that resulted in complete shutoff of water flow through the fracture. In addition, the thermal stability of CSC was successfully evaluated at 275°F.

NOMENCLATURE

CO_2 = Carbon dioxide
$CaCl_2$ = Calcium chloride
H_2S = Hydrogen sulfide
k = Permeability, mD
KCl = Potassium chloride
NaCl = Sodium chloride
NaOH = Sodium hydroxide
q = Flow rate, mL/min
SF = Swelling factor
T = Temperature, °F
TDS = Total dissolved solids
μ = Viscosity, cP
ΔP = Pressure drop along the core, psi

REFERENCES

1. Conformance Technology, Halliburton Publication F-3373, 1996.
2. Creel, P., Booker, J.: "Correcting Out-of-Zone Injection Problems on a Waterflood in SE New Mexico," paper presented at the 2007 SWPSC, Lubbock, Texas, April 2007.
3. Creel, P.G., Honnert, M., Kelley, R., Tate, R., Dalrymple, E.D.: "Conformance Water-Management Team Developments and Solutions on Projects in the Permian Basin," Paper SPE 70068 presented at the 2001 Permian Basin Oil and Gas Recovery Conference, Midland, Texas, 14–16 May.
4. DOE/BC/14991-7 (DE96001234), L.D. Hallenbeck, K.J. Harpole and M.G. Gerard: "Design and Implementation of a CO_2 Flood Utilizing Advanced Reservoir Characterization and Horizontal Injection Wells in a Shallow Shelf Carbonate Approaching Waterflood Depletion," pp 26-27, May 1996.
5. Griffen, L.G., et al.: "Identification and Implications of Induced Hydraulic Fractures in Waterfloods," Paper SPE 59525 presented at the 2000 Permian Basin Oil and Gas Recovery Conference, Midland, Texas, 21–23 March.
6. Creel, P.G., Honnert, M., Tate, R., Everett, D.: "Five Years of On-Going Conformance Work in the Central Mallet Unit CO_2 Flood in West Texas Yields Improved Economics for Operator," Paper SPE 101701 presented at the 2006 First International Oil Conference and Exhibition in Mexico, Cancun, Mexico, 31 August–2 September.

7. Vasquez, J., et al: “Laboratory Evaluation of Water Swellable Materials for Fracture Shutoff,” Paper SPE 111492 to be presented at the 2008 SPE North Africa Technical Conference and Exhibition in Marrakech, Morocco, 12–14 March.
8. Green, C., et al.: “Utilization of a Crystallized Hydrating Copolymer to Modify an Injectivity Problem in a Horizontal CO_2 WAG Injector in the South Cowden Unit, Ector County, Texas—Post Treatment Coil Tubing Acidizing Stimulation—Case History,” paper presented at the 2007 SWPSC, Lubbock, Texas, April 2007.

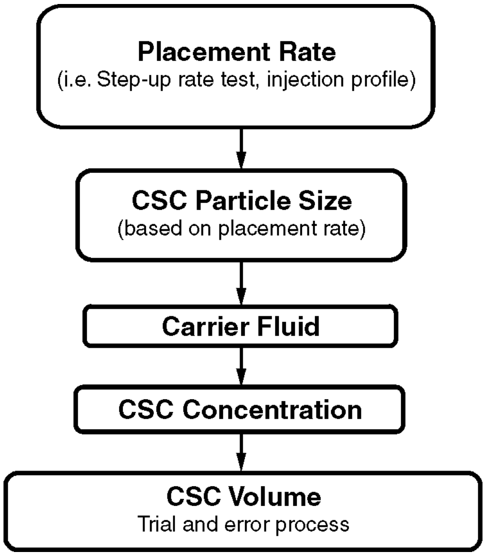

Figure 1—Crystallized Superabsorbent Copolymer Design Flow Diagram

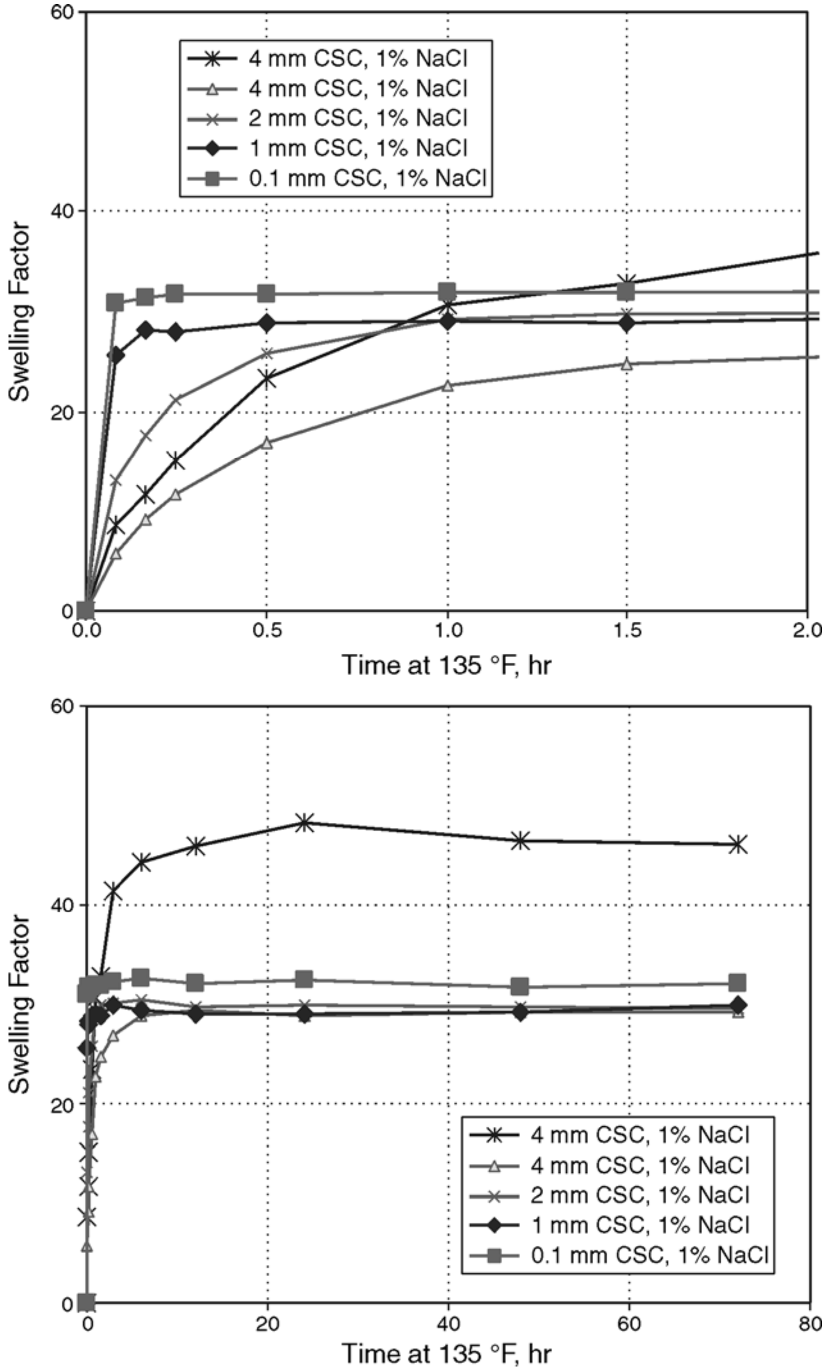

Figure 2—Effect of Particle Size on CSC Swelling Rate

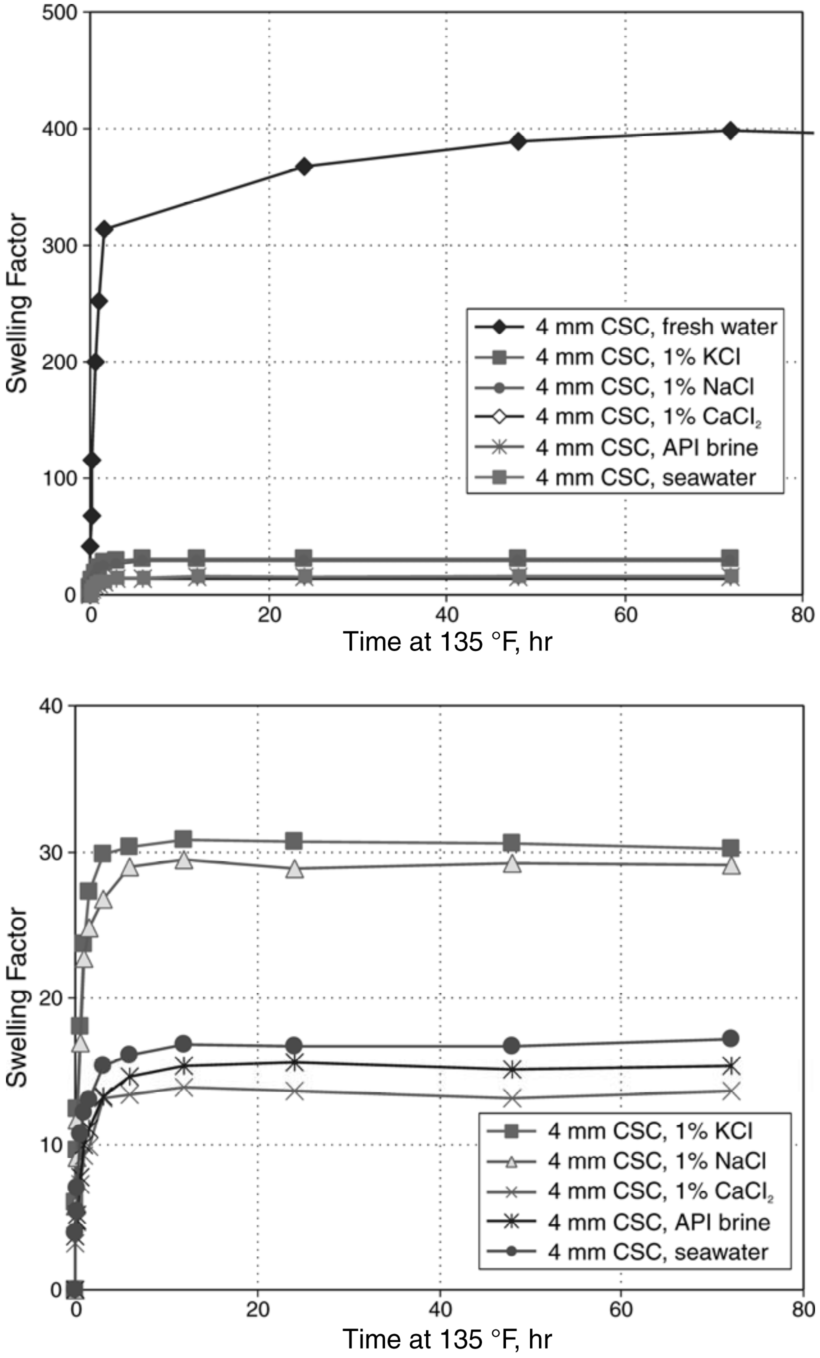

Figure 3—Effect of Different Mixing Waters on CSC Swelling Factor

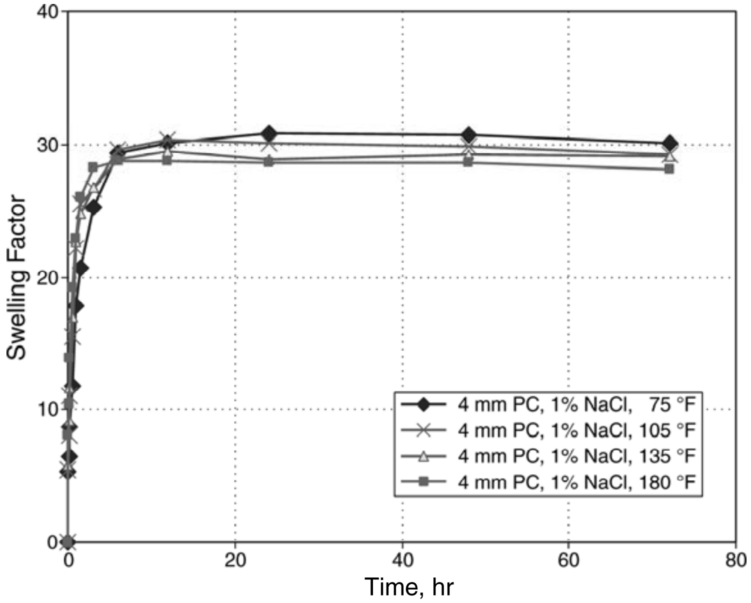

Figure 4—Effect of Different Temperatures on CSC Swelling Factor

Figure 5—Synthetic Core with Created Fracture

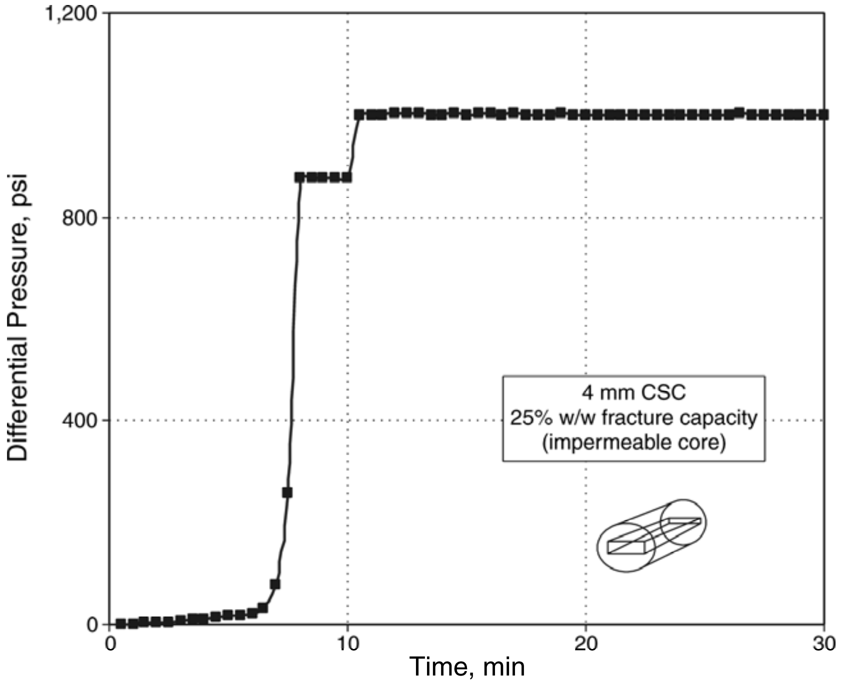

Figure 6—CSC, Extrusion Core Test Using a Synthetic Impermeable Core at 135°F

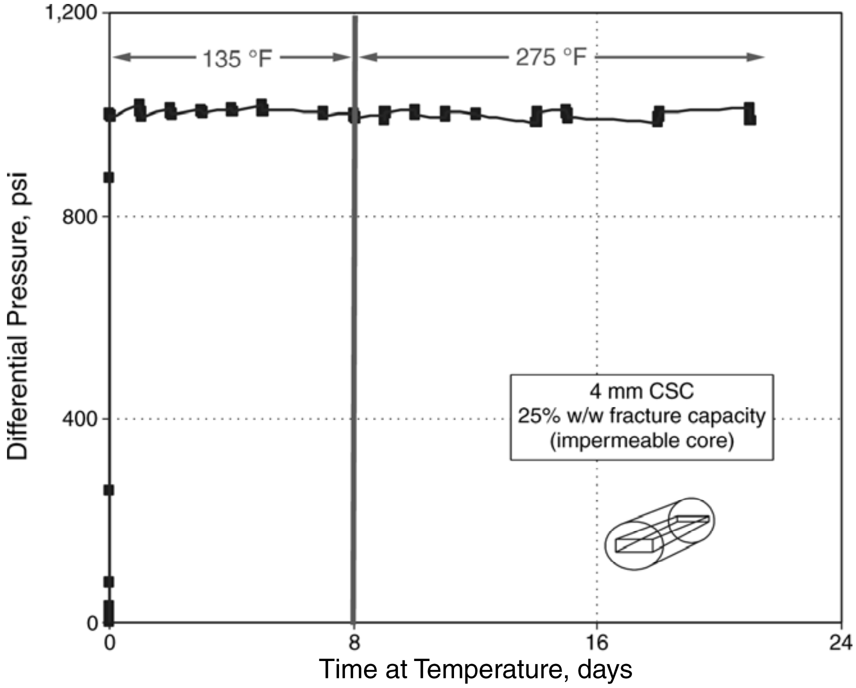

Figure 7—CSC, Extrusion Core Test Using a Synthetic Impermeable Core at 135°F And 275°F (After One Month)

Figure 8—Testing Cell for the H_2S and CO_2 Degradation Experiment

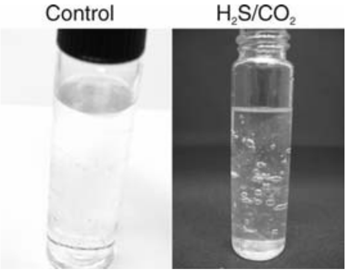

Figure 9—Summary of the H_2S and CO_2 Visual Degradation Tests with 165,000-Ppm TDS Brine Water at 135°F For CSC

Figure 10—CLAM with CSC Injector

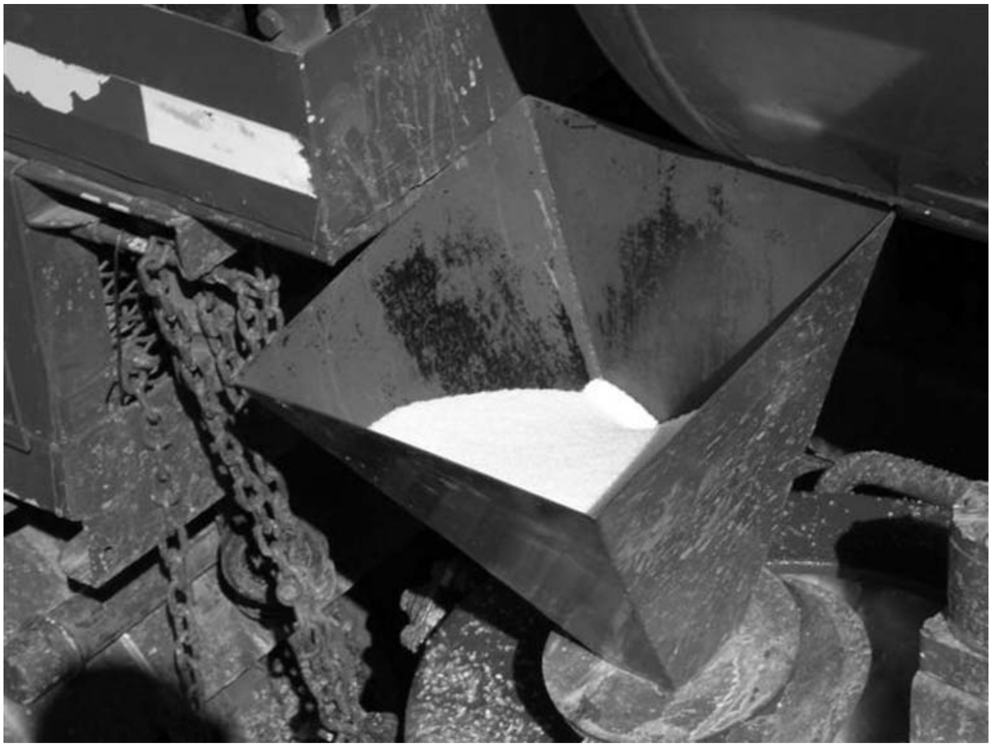

Figure 11—Injector

Figure 12—Injection Point