# USING CRYSTALLIZED SUPER ABSORBENT COPOLYMERS IN CONJUNCTION WITH CEMENT PRIMARY AND SECONDARY OPERATIONS— CASE HISTORIES

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#### ABSTRACT

Due to influxes of water encountered while attempting to gain consolidation around wellbores and/or their tubulars, cement can have difficulty achieving the required sealing necessary for zonal isolation. High influxes of water present across areas needing remediation can cause the cement to deteriorate at any point from displacement through the time it takes it to form and develop enough strength to resist the process of deterioration.

Presented are results of trials, techniques developed, and results based on incorporating crystallized co-polymer super absorbent (CSA) materials mixed with cement and also as a preflush system in conjunction with cementing operations to address a variety of influx problems around wellbores.

Data includes laboratory analysis and performance evaluations generated while testing and performing these cement operational solutions. Diagnostics used to arrive at a best fit solution are also detailed and discussed.

#### **INTRODUCTION**

Water and  $CO_2$  water-and-gas (WAG) flood units in southeast New Mexico and the Permian Basin of west Texas often have a high influx of crossflows consisting of both gas and water that can damage cement used to promote consolidation during squeeze work or on primary operations. Influxes of fairly high rates are often witnessed and may have pressures influenced by local reservoir injection for miscible flooding.

Often conditions of many shallow dolomitic formations such as the San Andres, Grayburg, Glorieta, Paddock, and others of the Permian Age are highly eroded and contain rapid interwell communication caused by years of water and  $CO_2$  WAG flooding. Most of these formations were deposited in shallow-shelf carbonate environments along the western shoulder of the Central Basin in west Texas and southeast New Mexico. Natural fractures and karsted intervals often dominate the injection paths and can be very directional. Variations in the content of anhydrite within the dolomitic formations also exhibited differences in stresses and integrity to withstand injectivity. These layered, highly dolomitic reservoirs display significant permeability variations and porosity variances.

Variations in permeability and porosity are complicated for these formations because of their layered nature, with the content of anhydrite ranging from a small percentage to being the dominant rock content. These formations are characterized by multiple layers with discontinuous areas caused by widespread impermeable layers. Most of the current recovery in the western platform is attributable to pressure maintenance through waterfloods 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 7,000 ft.

Conditions in lithology, rock structure, and geological histories can limit the ability to achieve a balanced flood in the aforementioned reservoirs of SE New Mexico and west Texas due to the rock properties and architecture existing within their shallow dolomitic reservoirs. Fractures, fissures, and highly eroded, permeable formations may exist due to these naturally occurring conditions or can be caused by operational practices and outdated completion methods. These formation architectural conditions can lead to near-wellbore losses of integrity and requirements to perform squeeze work to regain zonal isolation.

Recent research and conformance applications on these WAG floods using dehydrated crystallized copolymer (a proprietary material consisting of dehydrated CSA for conformance designs), has been implemented to control the loss of injection fluids into interwell losses and high communication aspects during the floods. These designs are based on injectivity log profiles, formation reservoir characterization studies, and analyses of the issues regarding step-function changes needed to accomplish the development of redirecting the floods and blocking off interwell communications.

Using the CSA technology to address the highly invaded conformance applications has led to CSA use in cement squeeze designs to address near-wellbore conditions where a need to rapidly remediate influxes of water was required. This paper presents the ongoing work and processes/methods used in the squeeze work. The focus was to develop a system capable of changing slurry properties rapidly during their transition time to offset the influx of water to help preclude diluting and washing the slurry away before it sets.

#### PROBLEMS CONFRONTED

Identification of large influxes of water can often be observed while well returns and pressure builds during well shut-in time. Other times, the influxes are crossflows from higher-pressured intervals losing fluid into depleted intervals and exposed communication paths. These situations may often be obscured at the surface because they occur downhole. Historic results and knowledge of certain areas often aids the recognition that imbalance and influx problems are present.

Most formations in units characterized by imbalances and crossflows are under treatment by water or  $CO_2$  WAG flood. Layers with discontinuous areas caused by widespread impermeable layers can also lead to these imbalances. Adjoining formations are often not separated by any barrier and can communicate readily. Often, problems displaying interwell communication and high influxes are first noticed because of cycling problems with one or more of the injection well's offsetting producers. The direct communication between injectors and producers is referred to as cycling and manifests itself as a sudden spike in injectant-production volumes in producers shortly after the injection cycle begins.

An increase in injectant-production volume is usually accompanied by a decrease in oil-production volume. Another flag used to identify problems is that offset wells may not perform based on pressure support when injectivity has been lost to another zone not connected to the desired interval. Working on these wells to gain near-wellbore integrity can be very difficult due to their dynamic conditions of imbalances and high influxes of gas and/or water. Wellbore losses and lack of integrity usually display similar conditions with a potential for water influxes and crossflows 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 near-wellbore conditions. Hazardous conditions also exist with the presence of  $H_2S$  and iron sulfide content. Existing conditions and the physical nature of the problem should be addressed when defining the attributes and capabilities of a proposed solution; the solution's placement capabilities and required controls should also be defined.

When the conditions that lead to difficulty in gaining near-wellbore integrity exist, these conditions usually lead to additional problems, such as increased near-wellbore corrosion, loss of wellbore integrity, and difficulty in maintaining mechanical controls such as packer seals.

Along with determining the extent and condition of the near-wellbore problem of lack of integrity, there should be an opportunity for determining the required criteria of the treatment solution and the placement technique that should be used. Various placement methods exist and can be designed into the plan. Maximum injection pressure can be determined for bullheading the treatment fluids based on the integrity problems identified. Differential pressure responses may indicate the tortuosity aspects of fluid entry into specific portions of the reservoir and whether fluid is communicating back into the wellbore.

#### FRACTURE CONDITIONS

On wells where identified problems consisted of fracture and vugular communications aspects, treatments utilizing a crystallized copolymer system were performed. These materials were used to address fracture and fissure communication to keep these highly communicating features from thieving most of the injection and transmitting it almost directly into offset producers. The crystallized copolymers used are resistant to degradation by  $CO_2$  and

bacteria and have a temperature range of  $70^{\circ}$  to  $250^{\circ}$ F. Placements were made down current injection tubulars working rigless, a practice that can save expense by avoiding the need for a workover unit. Removal of the crystallized copolymer could then be obtained by reactions from bleaches or oxidizers, if needed.

#### Eroded Voids and Behind Casing Communication

Due to conditions affecting the primary cementing operations, often annular voids were left behind filled with either old mud cake or drilling solids. Where annular conditions are open, the existence of crossflows and future corrosion effects are greater. Often, these annular voids cause problems with production if communication exists from zones charged-up with water being free to flow into other intervals under hydrocarbon production. Often these vertical annular crossflow conditions are referred to as "elevators" by operators.

#### Solution Development – Testing Crystallized Slurry

As in any solution development, the conditions that exist should be addressed in creating a solution. The initial inclination has to be to create a solution with considerations that thoroughly identify the problem and the conditions in which it exists. Solutions should be considered and offered only after thoroughly analyzing a problem or need, usually by laboratory analysis that can simulate the well's conditions. Often, operators or service companies choose a solution without considering the well conditions simply by choosing to pump a volume of cement slurry with only consideration of the cement's lab-tested strengths, pump times, viscosity, and fluid loss numbers.

Based on the parameters of existing high water-influx conditions; the solution should have these attributes:

- 1. Ability to change setting characteristics rapidly during transition
- 2. Ability to possibly keep the same strength characteristics as the base slurry
- 3. Ability to gain strength characteristics if slurry additives could have an effect on internal filtrate content
- 4. Ability to withstand any influx of water during the transition stage (safety feature)

Laboratory analysis was performed and determinations were made using a crystallized copolymer in a super absorbent form.

#### Laboratory Analysis

Crystallized copolymer super absorbent (CSA) is water-swellable (but not water-soluble), 100% crystalline synthetic polymer. It absorbs hundreds of times its own weight in water ranging from 10 to 800 times based on the particular grind, carrier and present aqueous fluid, and the specific manufactured base material. The CP materials used in this study were intended for use primarily as a lost-circulation material and to address near-wellbore remediation problems and reservoir architectural features needing modification by cementing zonal isolation and conformance. These materials have been used successfully to address fracture and fissure communication in wells in nearby units to stop these highly communicating fracture features from thieving the majority of injection and transmitting almost directionally into offset producers.<sup>1</sup>

The CSAs currently used are sodium acrylate-based polymers that have a three-dimensional, network-like molecular structure. The polymer chains are formed from the joining of millions of identical units of acrylic acid monomer that has been substantially neutralized with sodium hydroxide (caustic soda).

Crosslinking chemicals tie the chains together to form a three-dimensional network, or 100% crosslinked system. This enables CSA to absorb water or water-based solutions into the spaces in the molecular network, forming a gel and locking up the liquid. The chemicals tie the chains together to form a three-dimensional network. This enables CSA to absorb water or water-based solutions into the spaces in the molecular network, forming a gel-like solution and locking up the liquid in suspension.

As the copolymer areas are being developed (manufactured) under temperature, it is put into a reactor and crosslinked while still under temperature until a certain viscosity is reached. It is then run through an extruder and out onto a mesh belt where it hardens. It is then sent to the chopper where it is cut to a specific size and bagged. The crosslinked process will help keep it insoluble.

The crystallized copolymers are resistant to degradation by  $CO_2$ , bacteria, and temperatures below 250°F. In addition, rigless placements can be made down current injection tubulars, which results in a savings by eliminating

the need for a workover unit. If the crystallized copolymer should require removal, it can be removed by reactions from bleaches or oxidizers generally placed with a coiled tubing unit.

In the current study, cement squeezes were considered when fractures were identified as potentially very open and not tortuous. With a high display of influxing water, all cements could be diluted and dispersed to cause a failure.

Crystallized copolymers will start to hydrate after 20 minutes if in fresh water and at temperatures below 110°F. Use of produced salt brines (8.9–9.2 lb/gal) can result in a delay of around 45 minutes before the crystals hydrate; placement may be defined around this feature. Once placed into the filtrate or cement slurry body, the squeeze treatments may be closed in for 30 minutes to allow the crystallized copolymers to begin to absorb water filtrate within the slurry. Once the squeeze is placed, it can then be allowed to go through the loss of water filtrate within the slurry, then have a squeeze pressure placed on it.

Ideally, a loss of filtrate within the slurry body gives it different properties such as denser slurry would have. An example: losing 25% of the filtrate on a 14.8-lb/gal cement slurry with a mix water ratio of 6.33 gal/sk would result in a loss (tying up) of 1.59 gal/sk of its mix water resulting in a slurry imitating a 16-lb/gal mix with 4.76 gal/sk remaining mix water. This would result in slurry changing its set time and also possibly gaining a final set strength of more dense slurry.

#### **Quality Control**

Laboratory analysis was performed to determine the set times and viscosity performance for the slurries in a range of mix densities and a variety of additives. **Table 1** shows analyses results for various cement blends and their setting times along with various other parameters to determine the capability to actually withstand the effects of influxing water on performance. As can be seen in Test 1 and Test 3, the use of CSA greatly affects the set time along with the final set strength. The set time was accelerated by 2 hours while the final set strength was doubled by using CSA.

#### CASE HISTORY

Presented is an example of the techniques and upfront evaluations used to address squeezing with this additive and results from these tests. The problem presented was excessive water production. This was believed to be due to a fracture developed during a 1976 interface job using 28,000 lb of 100-mesh sand in gelled water as a diverter with 18 bbl/min total rate. A 2005 conformance attempt to squeeze the open hole with 300 sks foamed cement then restimulating with foamed acid was marginally successful, reducing water production from 750 to around 550 BWPD but causing an oil loss that was gradually recovered.

In December 2006, water production increased to about 950 BWPD with fluid above pump almost to surface and no oil production. Based on experience in other wells, it was believed that this conformance problem could be solved by pumping a large volume of cement and being less aggressive with the re-stimulation. Production logging indicated 2,600 bbl/day flow (combined oil-water-CO<sub>2</sub>) with major CO<sub>2</sub> entry just below the casing shoe and major fluid entry from the same mid-pay fracture (~4,820 ft) that had previously been identified. The  $CO_2$  entry was in an anhydrite zone and believed to be fracture communication with a  $CO_2$  injector one pattern NW of this well. Three treatments were performed on this well. The first treatment was 200 sks cement and 500 sks foamed cement. While drilling out this squeeze, a significant CO<sub>2</sub> inflow was encountered just below the casing shoe. After confirming there was hard cement below the inflow interval, a squeeze with 4,300 lb copolymer was pumped, with the intention of a followup cement squeeze. The followup cement squeeze was not performed due to inability to pump into the well. While drilling out the new open hole, another gas influx was experienced. A treatment was designed to squeeze 100 sks of cement carrying 1 lb/sk of CSA, followed by 150 sks of an as yet unpatented blend. After gaining a significant pressure build (the job was switched to flush when pressure exceeded 2,500 psi), the cement was drilled out with no pressure or flow problems. The well was re-perforated and a gelled acid job and scale squeeze treatment were performed. The well "came in" with high pressure and significant CO<sub>2</sub> production. The initial wellhead pressure was 1,400 psi with the first two flow tests showing 30 BOPD, 20 BWPD, and 800 Mcf/D gas. Production logs indicated that the treatment was successful in squeezing off the major gas entry at the casing shoe, and the major water entry from the fracture developed during the 1976 interface job. Gas production has fallen over time, which may be an indication that high initial CO2 production was due to storage effects caused by crossflow from the fracture communication at the casing shoe down into the main pay. While it is not certain that the combination of CSA and cement was the definitive solution to conformance problems with this well, the fact

remains that the well was not brought under control until the CSA-cement job was pumped. Post-job production results indicate a successful job.

Many additional jobs with CSA mixed in cement or pumped ahead of cement have been performed. The repeated trend is significantly accelerated pressure build compared to similar wells where CSA materials were not utilized. The most significant comparison is in injection wells experiencing significant losses below the oil-water contact. Two procedures utilizing cement without CSA pumped 100 sks in two 50-sk stages, compared to procedures with a CSA lead and 25 sks of cement, achieving "lock-up." The results of these procedures with and without the CSA were similar. With the benefit of experience, the decision to use CSA is often based on pre-job pump-in pressure-rate behavior, with relatively low pressure indicating the need for CSA lead or CSA included in the cement mix. There remains a fairly lively debate over the merits of CSA mixed in cement compared to CSA as a lead stage to the cement. At this time it appears that either approach can be effective, and only further experience with both procedures can determine whether one approach is superior to the other. Regardless of the design (mixed with cement or lead stage), experience indicates that inclusion of CSA is highly successful in facilitating pressure build and rapid cement set while attenuating water influx and crossflow problems in the near-wellbore regime.

It is very important to note that the case histories discussed in this paper were in relatively low-permeability San Andres reservoirs, where the primary conformance problem is believed to be fracture communication in a limited channel. This procedure may not be the correct solution for reservoirs with large voids and vugular communication (for example, Canyon Reef reservoirs). Expressing this difference simplistically, the San Andres fracture communication could be equated to sealing a garden hose, while a reservoir with significant voids would involve filling up a river channel. Clearly, the CSA-cement solution is well suited to accelerating cement set time and sealing off near-wellbore conformance problems. In a reservoir with very high permeability and significant void space, this solution could lead to a false sense of success because the near-wellbore repair would be bypassed by high permeability and void space in the reservoir beyond the near-wellbore effects.

#### CASE STUDY RESULTS

The squeeze treatments were performed in a manner using the slurry's lab tested features addressing a rapid transition set quickly following placement and the initial squeeze pressure being placed on the cement. Post-treatment profile logs were run to determine whether the desired objectives had been accomplished (**Figure 1**).

#### **CONCLUSIONS**

Based on the successful results from work addressing this squeeze technique, problems associated with high water influx challenges are being addressed. The combination of CSA with cement appears to be a valuable tool in dealing with water influx and crossflow in near-wellbore conformance work. This combination has been successful both when CSA are mixed with the cement and with CSA as a lead stage for conventional cement.

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#### **REFERENCES**

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# Table 1—Lab Results Showing Different Cement Slurries with CSA

### Lab Test 1

Depth: 4,600 ft	Slurry Inf	ormation:	Water Amt:	6.32 gal/sk
BHCT: 95°F	Premium p	lus mixed with:	Density:	14.8 lb/gal
Job Type: Squeeze	11b/sk	CrystalSeal 4mm	Yield:	1.35 ft <sup>3</sup> /sk
Base Cement: Cemex	1%	CaCl <sub>2</sub>		
Water: Lab Tap				

## **Consistency Information**

## **Compressive Strengths**

Time	Temp	Pressure	Consistency	Time	Unit	Temp	Strength, psi	Method
1:30	95°F	3,700 psi	70 Bc	12	hr	95°F	1,650	UCA
				24	hr	95°F	2,150	UCA
				72	hr	95°F	2,875	UCA

Lab Test 2						
Depth: 4,600 ft	Slurry Inf	Slurry Information:				
BHCT: 95°F	Premium p	olus mixed with:	Water Amt: 12.6 gal/sk			
Job Type: Squeeze	1 lb/sk	CSA 4mm	Density: 12.5 lb/gal			
Base Cement: Cemex	10 lb/sk	Expansive additive	Yield: 2.27 ft <sup>3</sup> /sk			
Water: Lab Tap	1 lb/sk	Latex cement				
	0.50%	Density reducer				
	0.50%	Friction reducer				
	0.25 lb/sk	Defoamer				

Consistency Information			Compre	Compressive Strengths				
Time	Temp	Pressure	Consistency	Time	Unit	Temp	Strength, psi	Method
2:30	95°F	3,700 psi	70 Bc	12	hr	95°F	309	UCA
				24	hr	95°F	463	UCA
				72	hr	95°F	899	UCA
Lab Tes	st 3							
Depth: 4,600 ft Slurry Inf			ry Information	:		Water Amt	6.32 gal/sk	
BHCT: 95°F Premium p			nium plus mixed	blus mixed with: Density: 14			14.8 lb/gal	
Job Type:	Squeeze		1%	$CaCl_2$			Yield	1.35 ft <sup>3</sup> /sk
Base Cen	nent: Cemex							
Water: La	ab Tap							

Consistency Information			Compressive Strengths					
Time	Temp	Pressure	Consistency	Time	Unit	Temp	Strength, psi	Method
3:30	95°F	700 psi	70 Bc	12	hr	95°F	714	UCA
			24	hr	95°F	980	UCA	
			48	hr	95°F	1,310	UCA	



Figure 1 - LLU 401 pre-job and post-job production profiles. Log on left is pre-treatment; log on right is post treatment. It appears that the large gas entry at the top of Zone 8 was eliminated, along with the high-volume fluid entry from a fracture extending down from 4,830 ft. Pre-treatment "rate" is 2,600 BWPD, while post-treatment "rate" is 40 BOPD, 100 BWPD, 500 Mcf/D CO<sub>2</sub>. "Rate" is based on velocity shots at downhole pressure.