



Review Paper

Examination of literature on colloidal dispersion gels for oil recovery

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ABSTRACT

This paper examines literature that claims, suggests, or implies that floods with “colloidal dispersion gels” (CDGs) are superior to polymer floods for oil recovery. The motivation for this report is simple. If CDGs can propagate deep into the porous rock of a reservoir, and at the same time, provide resistance factors or residual resistance factors that are greater than those for the same polymer formulation without the crosslinker, then CDGs should be used in place of polymer solutions for most/all polymer, surfactant, and ASP floods. In contrast, if the claims are not valid, (1) money spent on crosslinker in the CDG formulations was wasted, (2) the mobility reduction/mobility control for CDG field projects was under-designed, and (3) reservoir performance could have been damaged by excessive loss of polymer, face-plugging by gels, and/or excessive fracture extension.

From this review, the clear answer is that there is no credible evidence that colloidal dispersion gels can propagate deep into the porous rock of a reservoir, and at the same time, provide resistance factors or residual resistance factors that are greater than those for the same polymer formulation without the crosslinker.

CDGs have been sold using a number of misleading and invalid arguments. Very commonly, Hall plots are claimed to demonstrate that CDGs provide higher resistance factors and/or residual resistance factors than normal polymer solutions. However, because Hall plots only monitor injection pressures at the wellbore, they reflect the composite of face plugging/formation damage, in-situ mobility changes, and fracture extension. Hall plots cannot distinguish between these effects—so they cannot quantify in situ resistance factors or residual resistance factors.

Laboratory studies—where CDG gelants were forced through short cores during 2–3 h—have incorrectly been cited as proof that CDGs will propagate deep (hundreds of feet) into the porous rock of a reservoir over the course of months. In contrast, most legitimate laboratory studies reveal that the gelation time for CDGs is a day or less and that CDGs will not propagate through porous rock after gelation. A few cases were noted where highly depleted Al and/or HPAM fluids passed through cores after one week of aging. Details about these particular formulations/experiments were sparse and questions remain about their reproducibility. No credible evidence indicates that the CDG can propagate deep into a reservoir (over the course of weeks or months) and still provide a greater effect than that from the polymer alone.

With one exception, aluminum from the CDG was never reported to be produced in a field application. In the exception, Chang reported producing 1–20% of the injected aluminum concentration. The available evidence suggests that some free (unreacted) HPAM and aluminum that was associated with the original CDG can propagate through porous media. However, there is no evidence that this HPAM or aluminum provides mobility reduction greater than that for the polymer formulation without crosslinker.

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1. Introduction

This paper examines literature that claims, suggests, or implies that floods with “colloidal dispersion gels” (CDGs) are superior to

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polymer floods for oil recovery. More specifically, we examine whether colloidal dispersion gels can propagate deep into the porous rock of a reservoir, and at the same time, provide resistance factors or residual resistance factors that are greater than those for the same polymer formulation without the crosslinker.

The motivation for this report is simple. If CDGs can propagate deep into the porous rock of a reservoir, and at the same time, provide resistance factors or residual resistance factors that are greater than those for the same polymer formulation without the crosslinker, then CDGs should be used in place of polymer solutions for most/all polymer, surfactant, and ASP floods. In contrast, if the claims are not valid, (1) money spent on crosslinker in the CDG formulations was wasted, (2) the mobility reduction/mobility control for CDG field projects was under-designed, and (3) reservoir performance could have been damaged by excessive loss of polymer, face-plugging by gels, and/or excessive fracture extension.

For thousands of years, humans have recognized that particulates are removed by flow through porous media. That is why we have clean drinking water. So, it seems reasonable to question whether particulates (e.g., gel particles) can propagate deep into reservoir rock and still act as a viable mobility-control agent.

This manuscript will first discuss papers that question the utility of CDGs. Next, papers will be examined that advocate CDGs. The next section examines field applications of CDGs. Finally, brief comments are provided about simulation of CDG performance in porous media and a contrast with “in-depth profile modification.” In all cases, we focus on whether colloidal dispersion gels can propagate deep into the porous rock of a reservoir, and at the same time, provide resistance factors and/or residual resistance factors that are greater than those for the same polymer formulation without the crosslinker.

2. Laboratory papers questioning the viability of colloidal dispersion gels (CDGs) for oil recovery

This section summarizes papers that present laboratory evidence that “colloidal dispersion gels” behave like other gel systems used in oilfield applications. Specifically, when the formulation is a “gelant” (i.e., before polymer crosslinking reactions proceed to the point where gel aggregates grow to approach the size of pore throats), the gelant propagates through porous rock like a polymer solution without the crosslinker. After gel particles grow to approach the size of pore throats (i.e., “gelation”), the “gel” no longer propagates through porous rock at a practical rate. Further, like other oilfield gel systems, the “gelation time” is relatively short—typically a day or less. Consequently, colloidal dispersion gels cannot be expected to flow deep into a reservoir like a polymer flood. It will not provide a cheap or improved substitute for a polymer flood.

Walsh et al. (1983) investigated an early version of the aluminum-citrate-HPAM process, where the crosslinker and polymer were injected in alternating slugs. They noted that injected aluminum was not produced from some cores even after twenty pore volumes of injection. The delay in aluminum propagation was attributed to aluminum hydroxide precipitation. Their experiments revealed that aluminum precipitation could be eliminated by using large ratios of citrate to aluminum. However, even at large ratios, there are still unresolved concerns about precipitation over longer time periods characteristic of reservoir floods.

Rocha et al. (1989) investigated aluminum and citrate retention on silica sand as a function of (1) aluminum concentration (0.3–97 ppm), (2) Al/citrate ratio (1.5–2 mol/mol), and (3) velocity in porous media (1–10 ft/d). Aluminum retention increased with increased aluminum concentration, with increased aluminum/citrate ratio, and with decreased velocity in porous media. An average

value of aluminum retention for 58 experiments was 18 $\mu\text{g/g}$ (weight of aluminum retained per mass of rock). Retention of citrate increased with increased citrate concentration and with increased Al/citrate ratio. An average value of citrate retention for 20 experiments was 49 $\mu\text{g/g}$. For comparison, Spildo et al. (2010) later reported an aluminum retention value of 4.5 $\mu\text{g/g}$ in Berea sandstone.

The ability of aluminum to propagate into a reservoir can be estimated using a retention calculation (Eq. (1) of Manichand and Seright, 2014). If rock porosity is 0.2, aluminum retention is 18 $\mu\text{g/g}$, and aluminum concentration is 30 ppm, more than six pore volumes of aluminum solution must be injected to fill one pore volume of porous rock. Put another way, if a 0.1 PV bank of aluminum is injected into a well, the aluminum front will only penetrate 1.6% of the reservoir. If, aluminum retention is 4.5 $\mu\text{g/g}$, and aluminum concentration is 30 ppm, more than 1.6 PV of aluminum solution must be injected to fill one pore volume of porous rock. Put another way, if a 0.1 PV bank of aluminum is injected into a well, the aluminum front will penetrate 6% of the reservoir.

Seright (1994) examined propagation of a standard aluminum-citrate-HPAM formulation through Berea sandstone—and compared with the performance of the same composition without the aluminum-citrate crosslinker. This gelant contained 300-ppm Tiorco HiVis 350 HPAM and 15-ppm aluminum (as citrate Tiorco 677). In 707-md Berea, the gelant formulation exhibited the same resistance factor (effective viscosity in porous media) as the polymer solution that did not contain any crosslinker. However, 2 h after gelant preparation, the gelant crosslinking reaction proceeded to the point of gelation—so that the formulation could no longer flow through the rock. After gelation, the only fluid that continued to propagate was the brine from which the crosslinked polymer has been stripped. These results indicate that the aluminum-citrate-HPAM formulation basically behaves like other gels and gelants. Early in the gelation process, the gelant formulation propagates through sandstone like a polymer solution without crosslinker. After some point (presumably when gel aggregates grow to the size of pore throats), gel propagation is extremely slow or negligible. Thus, the aluminum-citrate-HPAM formulations do not propagate through porous rock like a “super polymer” after gel formation.

Stavland and Jonsbraten (1996) provided a paper that was primarily interested in whether aluminum citrate can be a viable substitute for chromium acetate as an HPAM crosslinker (because of environmental concerns about the use of chromium in Norway). Their work focused on high aluminum (200–3000-ppm) and polymer (3750–5000-ppm) concentrations in Berea and Bentheim sandstone cores. Injection rates were such that one pore volume was injected after 6 h or less. Even with these rates, high resistance factors and residual resistance factors were focused on the very front of the core in four of seven corefloods. In two of the seven corefloods, composite residual resistance factor for the cores were only 1.2 and 2.0 respectively—indicating little gelation. For the seventh core, which used 3000-ppm aluminum and 5000-ppm HPAM, a residual resistance factor of 2000 was reached. During all corefloods, they reported very high levels of aluminum retention (4000–56000 $\mu\text{g/g}$).

Ranganathan et al. (1998) published a classic paper on whether or not colloidal dispersion gels can propagate through porous rock. The work focused on formulations that contained 300-ppm HPAM (Tiorco HiVis 350) and 15-ppm aluminum (as citrate, Tiorco 677). Important statements from this paper were:

“In-depth in-situ flow resistance did not develop when the gelling solution was injected into the sandpacks at frontal advance rates of 2 ft/D. Propagation through the sandpack was

similar to a polymer solution. Flow resistance was characterized by the formation of a gelatinous filter cake, which formed when the injected solution encountered a change in flow medium, such as a screen placed at the ends to retain sand in place, the interface between the 50-mesh coarse sand layer at the inlet and the rest of the sandpack, and void spaces.”

“Delaying injection by 2 hours after mixing in-line (to simulate field conditions) resulted in severe front-end stripping of gel aggregates. In all cases, residual resistance factors for the gel solution were similar to those obtained with a polymer displacement alone. Effluent fractions from gel solution displacements never developed a gel structure, and their viscosities were significantly lower than the injected solution. In the study of gel size distribution, aggregates were not detected at reaction times of 4 and 8 hours.”

“In-depth permeability reduction was not observed. Resistance developed at the porous media inlet only. When propagated through porous media, the CDG loses all gel-like properties. The effluent solutions obtained during both the polymer and gel displacement experiments were found to have low viscosities and never formed a gel structure.”

“Aluminum was retained in significant amounts in the sandpacks.”

As a summary: Before CDG gel aggregates grow to approach the size of pore throats, CDG gelants can flow through porous media, exhibiting the same resistance factor as the polymer solution without crosslinker. After CDG gel aggregates grow as large of pore throats, they no longer propagate through porous rock. This behavior is characteristic of other gels (McCool et al., 1991; Eggert et al., 1992; Hejri et al., 1993; Todd et al., 1993; Midha et al., 1996; Cheng et al., 2005; Al-Assi et al., 2009). Further, the time at which gel aggregates grow to approach the size of pore throats is relatively short (typically less than 24 h).

Pritchett et al. (2003) focused on “Bright Water.” However, they stated that inability of aluminum to propagate was responsible for failure of an early version of the Bright-Water process that was applied on the North Slope of Alaska (Kuparuk). They also stated that “any permeability modification appeared to be primarily in the region of the injection well”—confirming the inability of the gel to propagate deep into the reservoir.

Seright et al. (2006) and Seright (2006a,b) performed two similar experiments with the same formulations in 493-md and 234-md Berea sandstones. These experiments tested the formulation’s properties at both high (143 ft/d) and low (2.7 ft/d) velocities in rock. The same conclusions were reached. Specifically, early in the gelation process, the gelant formulation propagates through sandstone like a polymer solution without crosslinker. After some point (presumably when gel aggregates grow to the size of pore throats), gel propagation is extremely slow or negligible. This paper demonstrates that the colloidal-dispersion-gel (CDG) process is not superior to normal polymer flooding. Colloidal dispersion gels, in their present state of technological development, should not be advocated as an improvement to, or substitute for, polymer flooding.

Seright et al. (2006) examined two baseless speculations that were advocated by vendors of CDGs. The first was the issue: **Does shearing of colloidal dispersion gels allow for effective, deep penetration?** The CDG vendor (Smith et al., 2000) speculated that when CDG gelants are sheared at high velocities in rock near a wellbore, gelation is delayed substantially (i.e., by weeks or months)—thus, allowing gelant to penetrate far into a formation

before developing high resistance when flowing at low velocities. This was pure speculation—no credible data was provided to support the suggestion. Seright et al. (2006) demonstrated that shearing CDG gelants through porous rock may delay gelation and development of high resistance factors by a few hours, but certainly NOT for days, weeks, or months, as speculated (without support) by the CDG vendor. A relatively short time after gelant preparation (8.2–8.9 h), the sheared CDG gel caused severe plugging and did not propagate through 196- to 234-md rock.

A second issue was: **Can CDG gels flow in porous media with permeabilities less than 8 darcys?** Presumably, formed colloidal dispersion gels (or any other gel) could flow through a porous medium if the permeability was sufficiently high or if the pressure gradient was sufficiently large. For an extreme example, if the porous medium consisted of packed bowling balls, we suspect that many gels could readily be extruded through. Reservoir strata have been reported that have matrix permeabilities between 1 and 10 darcys—where fractures, vugs, and fracture-like features are not present. So, we wondered whether formed CDG gels could enter and flow through a consolidated porous medium with a permeability up to 8 darcys—specifically using an 8-darcy porous polyethylene core that was 2.6 ft (78.4 cm) long, with four internal pressure taps. A colloidal dispersion gel was prepared that contained 300-ppm Tiorco HiVis350 HPAM, 15-ppm aluminum (as citrate, Tiorco 677), and 0.5% KCl. This formulation was aged for 1 day at 41 °C. Then it was injected into the core using a rate of 26 ft/d (400 cm³/h). Resistance factors in the first core section rapidly rose and exceeded 1000 during the first 0.08 PV of CDG injection. At this point (4 min after the start of injection), the throughput value for the inlet face was 2.2 cm³/cm², and the pressure drop across the first core section was 179 psi. Thus, the gel caused severe face plugging. In contrast, resistance factors for the other four sections of the core remained low—indicating no propagation of CDG gel beyond the first core section. Thus, 1-day-old colloidal dispersion gels do not flow through porous media with permeabilities less than 8 darcys.

Al-Assi et al. (2009) examined a gel system containing 1000 ppm polymer and 33.3 ppm aluminum citrate was studied in 10-darcy sandpacks that were 2 ft and 4 ft long. Consistent with other research, they reported that aluminum-citrate-HPAM (CDG) formulations can flow through porous rock until they grow to the size of pore throats. However, this time is not long enough to allow these aggregates to penetrate deep into a reservoir where most of the oil resides.

Jing et al. (2017) demonstrated the extrusion of 140–500 μm swollen/deformable gel particles through 13–50-darcy packs typically requires pressure gradients of at least 200 psi/ft—which is clearly not feasible for reservoir flooding (where pressure gradients are typically on the order of 1 ft/d and permeabilities are usually less than one darcy). They also demonstrated that the pressure gradient for gel particle flow through a pore throat increases dramatically with increased ratio of particle size to throat size. Similar findings were reported by Bai et al. (2007a,b), and Imqam et al. (2015, 2017). In agreement, Abdelfatah et al. (2017) performed an extensive modeling effort demonstrating that any viscosity development is unlikely when attempting to propagate gel particles through porous media.

Lenchenkov et al. (2019) measured the rate of “polymer nanospheres” through outcrop sandstones and concluded “Depending of the characteristics of the reservoir, the required deep propagation might not be realistic.” In less saline brines, nanosphere propagation was poor and impractical for a field application. In more saline brines 85% of the nanospheres could propagate through a core (meaning that 15% could not propagate even after injecting 60 PV). However, the resistance factor development was very small (i.e.,

resistance factor = 1.5) and of no practical value for fluid diversion or mobility control. Lafitte et al. (2018) also noted that a gelant based on nanoparticles concentrated on the injection portion of flooded cores.

3. Lab work that purports to support colloidal dispersion gels

Several papers describe laboratory studies that were intended to support the use of CDGs. The key question is whether any of those studies contradict the literature mentioned above. More specifically, do they provide evidence that CDGs can propagate deep into the porous rock of a reservoir and at the same time provide a resistance factor or residual resistance factor that is greater than that provided by the polymer solution without the crosslinker?

Smith et al. (2000) was commonly referenced by several papers that advocate use of CDGs. The paper describes the use of a “transition pressure test” which involves “flowing gels through a screen pack of five 100-mesh screens at several different pressures, to determine the pressure at which the gels resist flow through the screen pack to a greater extent than uncrosslinked polymer.” Interestingly, Figure 2 of the paper claims that seven days are needed for CDG gels (with 600–900-ppm HPAM and 30–45-ppm Al) to form. In contrast, less than one day is typically required for CDG gels to stop propagating through porous media (Seright, 1994; Rocha et al., 1989; Ranganathan et al., 1998; Seright et al., 2006; Al-Assi et al., 2009). Two observations are relevant here. First, Smith et al. (2000) did not report observations between 1 day and 7 days, so it seems possible that the gels may have actually formed much closer to Day 1 than Day 7. Second, it makes sense that a longer time would be needed for gel aggregates to grow large enough to clog a 100-mesh opening (150 μm) than a typical rock pore throat (10–50 μm).

A number of core experiments were performed using a CDG formulation with 700-ppm DQ12 HPAM (12 million g/mol Mw, 20% hydrolysis) with 17.5-ppm Al (as citrate) at 45 °C. For the experiments where resistance factors and residual resistance factors were reported, the paper states: “The injection strategy was such that CDG was never aged more than 2.5 h when the last of the CDG moved through the sand face. CDG was injected for 1–2 h, beginning with the highest flow rate then decreasing to the lowest flow rate in increments, with at least 2 PV of CDG injected. Thus, most of the CDG placed in the cores had moved through at the highest flow rates.” During 2.5 h of injection, resistance factors for CDG were the same or less than for polymer solutions (without crosslinker). This result was not surprising and was quite consistent with observations by others (Seright, 1994; Rocha et al., 1989; Ranganathan et al., 1998; Seright et al., 2006; Al-Assi et al., 2009). Before the gelation time, the CDG gelant acts the same in porous media as the polymer solution without crosslinker.

The cores were shut in after gelant injection filled the cores. After the gelation time, water was injected to determine residual resistance factors. Residual resistance factors in a ~3000-md core were found to range from 28 to 37 for CDG and around 7 for polymer solution without crosslinker. In a ~1000-md core, residual resistance factors were found to range from 55 to 63 for CDG and around 14 for polymer solution without crosslinker. The fact that residual resistance factors for CDG were higher than for the polymer solution is not surprising—because the CDG gelant was quickly pushed all the way through the cores before the gelation reaction was completed. This type of behavior occurs with virtually all effective gelants/gels. However, if the CDG gelant only flows for ~24 h (or less) before gelation occurs in the porous rock, one cannot expect high CDG residual resistance factors far from the injection wellbore. Also, note that the residual resistance factors in 3000-md cores were less than in 1000-md cores—both for the CDG and the

polymer. This type of behavior has been reported very commonly for polymers, gels, and particulates (Hirasaki and Pope, 1974; Vela et al., 1976; Zaitoun and Kohler, 1987; Seright, 1992; Bai et al., 2007a,b). As expected, these materials reduce the flow capacity of less-permeable rock by a greater factor than high-permeability rock. Finally, we should mention that the reported residual resistance factors from this paper (especially for polymer) are excessively high because “a minimum of 2 PV” of water were injected after CDG or polymer placement. Because of the unfavorable mobility ratio during water injection, achieving a true residual resistance factor can require 100 PV or more (Seright, 2017). Even so, it is quite credible that a core filled with CDG should provide a higher residual resistance factor than a polymer solution. The more controversial issue is whether the CDG will propagate sufficiently far into a reservoir to provide a useable residual resistance factor. Another important issue is whether higher residual resistance factors in less-permeable zones will harm sweep efficiency (Seright, 2010).

The paper also reported results from experiments where three cores (permeabilities of ~300 md, ~1000 md, and 3000 md) were flooded in parallel. Apparently, these were oil displacement experiments. The paper concluded that the CDG flooded oil from this arrangement more efficiently than polymer solutions. However, a detailed examination of the data raises doubts whether that was true. For all three cores in the setup, recovery was always higher during polymer injection than during CDG injection. The claimed advantage for the CDG was gained exclusively during the water-flood after the chemical bank was injected. The value of this latter laboratory behavior to an actual field situation is questionable. With short laboratory cores (as used in the above laboratory study), diffusion and dispersion can readily compromise small gelant banks placed in the less permeable of the parallel cores—giving the false impression that gelant does not significantly enter or damage less-permeable oil zones (Seright, 1991a). In real field applications, the distance of gelant penetration is several feet or more, even in the least permeable oil-productive zones (Seright, 1988, 1991a,b; Nimir and Seright, 1996; Ye and Seright, 1996; Zhang and Seright, 2007). For these distances, diffusion and dispersion will not destroy gelant banks (Seright, 1991a).

Chang et al. (2006) described a pilot project at Daqing where they injected 0.179 PV CDG, then 0.155 PV 600-ppm HPAM, then 0.196 PV CDG. The CDG formulation contained 600–700-ppm HPAM with 20–25-ppm Al (as citrate). For the laboratory portion of this paper, an interesting shearing experiment was reported in their Table 5. The description of what was done in this paper was extremely limited. We can guess that this formulation contained ~600-ppm HPAM (12–17 million daltons) with 20–25-ppm Al (as citrate) in brine with either 599 or 1197-ppm TDS at 45 °C. But we don't know for certain because of omissions in the paper. The paper states that CDG injection was “at a rate that is comparable to the rates injected into perforations.” Their Table 5 implied that a 7-day old CDG formulation could flow through a 3000-md core and still provide a viscosity greater than 100 cp. We are not aware of anyone else ever observing results like these, so it would be helpful if we could reproduce them. It would be very useful to know (1) the exact composition of what was injected, (2) the flux at which the fluid was injected, (3) the behavior of a polymer solution with the same composition but no crosslinker, (4) whether the core was consolidated or a sand pack (which could allow gel bypassing if the sandpack was not packed properly), (5) whether any plugging was noted during any of the injections, and (6) whether the fluid lost polymer or aluminum concentration during any of the cycles. This would be a key experiment to repeat with additional measurements to address the issues just mentioned. Nevertheless, even if the results in Table 5 are accepted, the viscosity loss noted by 15

days could result from substantial amounts of aluminum and/or polymer being stripped from the formulation—i.e., a substantial loss of viscosity that is no longer available to propagate deep into the formation.

The paper reported very briefly on a study of biodegradation of HPAM and CDG formulations. Surprisingly, both CDG and HPAM solutions showed substantial degradation after only one week of contact with several organisms. The description was very brief and no mention was made of the mechanism of polymer degradation. Most previous studies indicated that microorganisms do not metabolize the HPAM backbone. It would be interesting to know more detail about Chang's work here. If the polymer actually lost most of its viscosity (e.g., from 20 cp to 3 cp) within seven days in the field application, one would expect the polymer flood to be ineffective.

Liu et al. (2000) provided a short laboratory paper that examined CDGs for a planned pilot project at Daqing (China). The work examined 800-ppm HPAM (12 million daltons, 25% hydrolysis) in "River Water" with 817-ppm TDS and with a viscosity of 25.6 cp. This was compared with a CDG with 800-ppm HPAM in "Produced Water" with 3836-ppm TDS, 8-ppm aluminum, and 200-ppm "additive S", and with a viscosity of 12.7 cp.

In the first set of experiments, "artificial" cores were used that were 64 cm long and 3×3 cm² in cross section. The core had two internal pressure taps that divide the core into three sections of equal length. Water/brine was injected after the 0.4 PV polymer/CDG bank.

During the first 0.4 PV of CDG injection, pressure in the first core section rose four times higher than during polymer injection. During subsequent water injection, pressures at the core inlet dropped by one-third for the polymer case but decreased only modestly for the CDG. This indicates substantial face-plugging caused by the CDG. Also, the pressures for the last two core segments remain significantly higher for the polymer case than for the CDG case. In direct contradiction to the statements made by the paper, this result indicates (1) the CDG did not propagate through the core very well, and (2) resistance factors and residual resistance factors (beyond the injection sand face) for CDG were significantly LOWER than those for the polymer solution.

In a second set of experiments, parallel linear corefloods were conducted using cores with permeabilities of 0.2, 0.6, and 1.8 μm^2 . The cores were saturated with water and oil (9 cp at 45 °C) and then waterflooded to 98% water cut. Next, 0.19 PV of polymer solution (same composition as mentioned above) was injected, followed by waterflooding to 98% water cut. Then, 0.19 PV of CDG (same composition as mentioned above) was injected, followed by waterflooding to 98% water cut.

As expected, the flow distribution in the three layers (H-high, M-medium, L-Low) improved during polymer injection. The H/M/L percentages went from 90.6/9.4/0 during water flooding to 63.3/26.6/10 during polymer injection. This improvement qualitatively demonstrates the benefit of polymer flooding. During subsequent water injection, the H/M/L distribution deteriorated to 93/6.3/0.7. This behavior also demonstrates basic fluid mechanics, as water forms viscous fingers through the polymer banks. During subsequent injection of the CDG, the H/M/L distribution improved to 74.8/19.4/5.8—which is better than the previous water injection but worse than the 63.3/26.6/10 ratio seen during polymer injection. So the sweep efficiency was clearly better during polymer injection than during CDG injection.

During the final water injection in the above experiment, the H/M/L flow distribution improved to 70.7/26.1/3.2. Presumably, this ratio resulted because of either gel formation in the cores or because of a diversion filtration effect at the inlet sand faces of the three cores. Concerning the former possibility, basic calculations

using the Darcy equation (Seright, 1988, 1991a,b) demonstrated that gels can improve flow profiles in parallel linear corefloods. However, this improvement in profile comes at a cost of significant reductions in flow capacity in all zones (including the less-permeable zones. Seright (1988) demonstrates that although an improvement can be seen after gelation during parallel linear corefloods, the flow profile is not expected to improve significantly for radial flow (i.e., in wells without fractures).

Concerning the second possibility (a diversion filtration effect), a comparison of Figures 9 and 10 of this paper suggests that formed CDGs or other particulates probably plugged the inlet sand face. This face plugging could occur on the inlet faces of all cores in a parallel flood, but the filter cake builds up most prominently on the inlet of the most permeable core. This particulate/filtration effect has been useful in providing diversion in matrix acidizing. However, since the particulates do not penetrate beyond the sand face, they have no value in improving the mobility ratio during a field polymer flood.

The paper states "The gel flooding still had 11.2% oil recovery increment after polymer flooding, which shows that the gel performance on in-depth blockage of higher permeability region was much better than in polymer solution." The part before the comma of this statement was true ONLY because more fluid was injected after the polymer flood. For the reasons mentioned above, the part of the statement after the comma has no valid basis.

Muruaga et al. (2008) described a field application (El Tordillo field in Argentina) where 18% PV CDG is applied after application of Marcit gel treatments. The Marcit gel treatments were stated as being directed at reducing channeling through fractures. In the laboratory portion of this work, the paper states "CDG's with polymer concentrations ranging from 300 to 1800 ppm were evaluated with polymer to crosslinker ratios from 20:1 to 40:1." We presume that the polymer was a high-Mw HPAM. The crosslinker was not stated. Presumably, it was either Cr(III)-acetate or aluminum citrate. Three CDG laboratory experiments are mentioned very briefly. First, gel strength and stability were examined using a "Transition Gel Unit". A CDG with 900-ppm polymer was found to indicate a gel after 24 h, but this gel was degraded after 1 week at 87 °C. Reaction with oxygen was speculated to be the cause of the degradation. Additional experiments were performed with oil, phosphonate, and other unspecified chemicals to examine gel stability. The results appeared inconclusive.

Another test involved injecting a CDG with 600-ppm polymer through 3 and 8 μm Millipore filters. This study was done to test "the hypothesis that the CDG's dehydrate as they pass through porous media, resulting in a significantly higher gel concentration in the reservoir compared to the injected concentrations." The paper claimed that "this hypothesis was confirmed" by their filter tests, and that "it appears that dehydration (leakoff) of water from the gelant may result in the formation of CDG's in reservoir conditions that cannot be detected by conventional laboratory analysis." No support or detail is provided for these statements. The obvious question is how these conclusions could have been reached from filter tests. It seems more likely that the filter tests confirm what other previous credible researchers have found with CDGs: after the gel forms, it does not flow any further through porous media under any normal reservoir pressure gradient (Seright, 1994; Rocha et al., 1989; Ranganathan et al., 1998; Seright et al., 2006; Al-Assi et al., 2009). The gels (which contain more than 99.9% brine) can dehydrate/concentrate when the crosslinked polymer is left behind on the filter, while brine leaves the gel and passes through the filter (Seright, 2003). If the gelation time is 24 h, the crosslinked polymer (in the form of gel particles that are larger than pore throats) cannot be expected to propagate further into the porous

rock of the reservoir after that time. If the Al or Cr crosslinker is stripped from the formulation (e.g., by retention in the rock), the polymer is free to flow onward through the reservoir and provide some polymer-flooding benefit. Any polymer that was tied up with the crosslinker would not propagate very far into the reservoir and would therefore be effectively wasted.

Xie et al. (2009) reported results from an NMR imaging experiment and a subsequent simulation study. Three cores were flooded in parallel—apparently with water, polymer solution, and “cross-linked polymer”. The cores had some level of mobile oil before flooding. A major problem with this laboratory study is that it provides no information about (1) the composition of the polymer or “crosslinked polymer” formulation, (2) whether the “crosslinked polymer” was a gelant or formed gel when injected, (3) whether the cores had any internal pressure taps, (4) whether any “crosslinked polymer” was produced, and many other experimental parameters. Although the paper claims that “cross-linked polymer flooding” recovered 13.9% more oil than water flooding, it is difficult to draw any conclusions from the experimental work. Like the laboratory work, the simulation effort did not describe many of the assumptions or conditions that were used in the effort. It appears that the authors simply assumed that cross-linked polymer solutions simply propagated like viscous polymer solutions in porous media. As mentioned in other parts of this review, this assumption is not correct.

Spildo et al. (2009) investigated CDGs that contained 600-ppm SNF 3630S HPAM and 30-ppm aluminum (as citrate). They argued that the size of the crosslinked particles increased with increasing molecular weight and concentration of the HPAM polymer. Sizes from 200 to 400 nm were found for CDG prepared in 0.2 wt% NaCl with 200–600 mg/g polymer and a polymer/aluminum ratio of 20:1. This observation is interesting because in a subsequent paper, Spildo et al. (2010) report that their aged (for 3–8 days) CDGs could flow through porous rock. This finding was in stark contrast to the behavior reported by others previously, using less-saline CDGs (Seright, 1994; Seright et al., 2006; Ranganathan et al., 1998; Al-Assi et al., 2009). It makes sense that Spildo's smaller, nanometer-sized CDGs can flow through porous rock, while previous CDGs could not.

Spildo et al. proposed a “log-jamming mechanism” to explain why their CDGs recovered more oil than waterflooding. We can't say that their mechanism is wrong, but we wonder why the “log jam” doesn't develop in the oil pathway as well as in the water pathway. Also, this paper did not compare experiments using CDGs with those where polymer without crosslinker was used. Since Xia et al. (2007) reported that HPAM solutions alone can reduce residual oil saturation below that associated with waterflooding, one wonders whether the effect reported by Spildo would have been seen to the same extent with polymer without crosslinker.

Spildo et al. (2010) examined a CDG with 600-ppm Flopaam 3630S and 30-ppm Al (as citrate) in either 1% NaCl or synthetic seawater. We note three key points from reviewing this paper. First, Spildo et al. reported that their aged (for 3–8 days) CDGs could flow through porous rock. This finding was in stark contrast to the behavior reported by others previously, using less-saline CDGs (Seright, 1994; Rocha et al., 1989; Ranganathan et al., 1998; Seright et al., 2006; Al-Assi et al., 2009). Spildo et al. reported that their procedure for preparing CDGs was different from previous researchers. They specify that they “pregenerated nano-size colloidal particles.” It makes sense that Spildo's smaller, nanometer-sized CDGs can flow through porous rock, while previous CDGs could not. A question is whether the nanometer size of Spildo's CDG particles was due to details of their preparation procedure or due to the higher salinity in which they were prepared.

A second point is that a substantial amount of aluminum was

stripped from solution by passing through the core. In their experiments, the effluent aluminum concentration never reached more than 40% of the injected concentration. Even though the effluent aluminum concentration was less than half that of the polymer, Spildo et al. chose to interpret their results as indicating “CDG propagate through water-wet Berea sandstone cores with no chromatographic separation. The CDGs are produced at a constant polymer-to-aluminum ratio that is significantly higher than the injected ratio. This indicates the presence of an excess of Al in the original CDG formulation.” They did not repeat their experiments and report results when the original CDG composition matched their hypothetical ideal Al/HPAM ratio. Consequently, it would be premature to dismiss the significance of aluminum retention from these experiments. Spildo et al. offered an aluminum retention value of 4.5 $\mu\text{g/g}$ in Berea sandstone. This value would be more convincing if they reported results where the effluent aluminum concentration reached the injected value. It is also interesting that Spildo et al. reported HPAM retention to be slightly lower for the CDG than for polymer solutions without crosslinker. Smith et al. (2000) claim that polymer retention from CDGs is substantially greater than from polymer solutions without crosslinker. Perhaps the small size of Spildo's CDGs (50–150 nm) was responsible for this difference.

Third, it is certainly conceivable that Spildo's nanometer-sized particles would not be filtered out by moderate-to-high-permeability Berea sandstone. However, that still leaves the question as to whether that suspension would provide a resistance factor or residual resistance factor that was greater than that for Spildo's 600-ppm HPAM formulation without aluminum. Pressure data from Figure 3 of their paper can be used to estimate resistance factors and residual resistance factors in the three sections of Spildo's Berea core.

Using this data, the table below lists resistance and residual resistance factors for the three core sections. Presumably, the second section provides the most reliable results because it is longest and not subject to end effects. The second section shows a resistance factor of 5.8 and a residual resistance factor of 1.8. Spildo did not report what the values would be for a polymer solution (600-ppm) without the crosslinker. However, the values in the table below seem quite consistent with what would be expected from a 600-ppm HPAM solution. So, it is not at all obvious that the CDG provided more resistance factor or residual resistance factor than the polymer alone.

We don't fault the specific conclusions listed by Spildo et al. in this paper. However, considering the central question of our project, the following observations must be added. First, aluminum retention during passing through the Berea core was substantial. Spildo's aluminum retention value of 4.5 $\mu\text{g/g}$ appears optimistically low since the produced aluminum concentration never exceeded 40% of the injected concentration. Second, Spildo's aged nanometer-sized CDG particles appeared to flow through Berea far more effectively than previous CDG particles. Nonetheless, it is not at all obvious that the CDG provided more resistance factor or residual resistance factor than the polymer alone.

Skauge et al. (2010) examined reductions in residual oil saturation during injection of (1) 300-ppm nanometer-sized silica without polymer (3 corefloods), (2) 300-ppm nanometer-sized silica with 300-ppm (1 coreflood) or 600-ppm HPAM (2 corefloods), (3) 300-ppm HPAM (1 coreflood), and (4) pre-generated CDG with 300-ppm HPAM and 10-ppm Al (as citrate) (1 coreflood). All formulations contained 0.5% NaCl. The floods with silica only did not reduce the oil saturation below the waterflood value. The flood with 300-ppm nanometer-sized silica with 300-ppm HPAM developed high pressure drops during injection but did not reduce the S_{or} . The two floods with 300-ppm silica and 600-

ppm HPAM reduced S_{or} between 21% and 24%. The flood with 300-ppm HPAM but no silica experienced some face-plugging but did not reduce the S_{or} . Finally, the flood with CDG (with 300-ppm HPAM and 10-ppm Al) “increased oil production by 5%”. The authors did not express the reduction in S_{or} in the same terms as was mentioned for the 600-ppm HPAM cases above. However, it appears that the S_{or} reduction was less than in the two experiments with 600-ppm HPAM and 300-ppm silica. Consequently, it is not obvious that the CDG was more effective at displacing residual oil than the polymer without crosslinker. More experiments would be needed to establish if there was a difference, within experimental error.

Guo et al. (2011) claimed that basically different mechanisms of oil recovery exist between polymer flooding and CDG flooding. The abstract states: “The injection capacity of the two processes are about the same, but polymer flooding features large injection increase amplitude, quick pressure increase in initial period and quick decrease for subsequent flooding pressure; while CDG injection features a slower and gradual increase and decrease. The oil recovery effect for polymer flooding is mainly realized during the process of polymer injection, featuring quick water cut decrease and fairly quick increase as well quick water cut increase for subsequent water flooding; the oil displacement effect of CDG is equivalent of that for polymer flooding during chemical injection, but performs much better than polymer during subsequent water flooding.” A detailed examination of the paper reveals that the above claims are unsupported and overly optimistic.

The paper presents results from parallel linear core floods using CDG injection in one case and polymer solution injection in another case. They plotted the fraction of flow that was produced from each of the three cores in a given experiment. In each experiment, they injected a sequence of 3 PV water, 3 PV oil, ~3 PV water, ~2 PV of either CDG or polymer solution, and finally 2 PV water at 45 °C. The CDG formulation contained 700-ppm HPAM (11.43 million g/mol, 26% hydrolysis) and 17.5-ppm aluminum (as citrate, TIORCO 677) in fresh water—providing a viscosity of ~20 cp at 45 °C. The polymer solution had the same composition without the aluminum citrate—and provided a viscosity ~22 cp at 45 °C. It is important to note that the CDG is no more viscous than the polymer solution without crosslinker.

In their Fig. 2, the “fractional flows” from the CDG and polymer experiments were virtually identical (1) during waterflooding before CDG or polymer, (2) during CDG or polymer injection, and (3) during the first 0.5 PV of waterflooding after CDG or polymer. This result is not surprising because the CDG was “injected within 1 h from the preparation”. Consistent with our work in 1994, the aluminum-HPAM reaction requires at least 2 h to form pore-plugging gels at this temperature. Consequently, the CDG simply acted like a polymer solution with no crosslinker during the CDG placement process. Also, we agree that the uncrosslinked CDG formulation is propagating through the cores at this time—because the CDG has not formed yet. The re-distributions of fractional flows during CDG and polymer injection were consistent with expectations. Polymer flooding is known to “improve the vertical injection profile”—i.e., shift part of the flow from the high-permeability core to the two less-permeable cores. Also, the shift in flow distributions during the subsequent 0.5 PV of water was in-line with expectations—i.e., they returned to the distributions that were in effect before CDG or polymer injection.

The big surprise in behavior occurs after 0.5 PV of water post-flush. After that point, CDG appears to substantially divert water flow from the 3000-md core into the 1000-md core (Fig. 2 above). How could that happen? The 0.5 PV water post flush should have flushed CDG from the 3000-md core at least as effectively as the 1000-md core (see Seright, 1991a). Smith et al. (2000) reported that

CDG residual resistance factors were found to range from 28 to 37 for CDG in a ~3000-md core and from 55 to 63 in a ~1000-md core.

There is a credible explanation for the final behavior in their Fig. 2. If the lines leading to the core inlets in their Fig. 1 were not flushed or cleaned after CDG injection, some CDG could have been present in those lines beyond 2-h after CDG preparation—at which time the Al-HPAM reaction formed gel aggregates sufficiently large to plug pore throats and not propagate through the cores. The CDG material then formed filter cakes on the inlet faces of the three cores. As with normal fluid diversion processes (e.g., use of particulates in matrix acidizing), the filter cakes grow to be largest on the inlet of the most-permeable core and smallest on the inlet of the least-permeable core. With sufficient injection of gel or particulate, the filter cakes would grow to a point where the flow is equalized in the cores—as was observed in the 1000-md and 3000-md cores in their Fig. 2. With sufficient additional CDG or particulate (of any kind), we expect that flow in the 300-md core could have also approached that for the two-more permeable cores. The problem from the viewpoint of a CDG flood is that CDG material does not flow through porous rock and provide mobility reduction deep within the reservoir. Consequently, their Fig. 2 definitely does not demonstrate or prove the merits of CDG over polymer flooding. If the experiment had internal pressure taps, we could have better distinguished between face-plugging/filter-cake-formation versus in-depth permeability reduction by the CDG.

In view of the surprising result during the last portion of water injection, there would have been considerable value in duplicating the experiment to determine if the results were reproducible. Without that, we can't accept the authors' interpretation.

Castro et al. (2013) and Manrique et al. (2014) described laboratory studies where CDG solutions contained 400–600-ppm HPAM with crosslinker ratios from 20:1 to 80:1 (5–30-ppm aluminum). The paper claimed that injection of fresh CDG formulation recovered more oil than a CDG formulation that was aged for 1 week. Castro et al. (2013) performed floods in 6-in.-long, 1.5-in.-diameter Berea sandstone cores with 23% porosity and 2-darcy permeability—suggesting a pore volume of 38.7 cm³. Given the rates indicated, the 6.5 PV of freshly prepared CDG was injected over the course of about 3.5 h. Castro stated that he injected 600-ppm polymer with 20:1 crosslinker (i.e., 30-ppm Al). Their Fig. 1a indicates that the polymer effluent stabilized at about 270 ppm, while the aluminum effluent stabilized at about 12 ppm. So, both polymer and aluminum experienced about 55% loss of concentration in passing through 6 inches of rock over the course of 3.5 h. In contrast, normal HPAM solutions (with no crosslinker) would reach full injected concentration within about 2 PV (see Manichand and Seright, 2014 and references therein). Consequently, it is difficult to imagine the fresh CDG (a) propagating very far into an actual reservoir and (b) providing viscosity (resistance factor) as desirable as that for the polymer alone.

Their Fig. 1b provides similar information for the same CDG, except that the CDG was aged for one week before injection. In this case, the polymer and aluminum experienced 75%–85% losses in concentration. These results indicate that additional crosslinking occurred between 3.5 h (i.e., Fig. 1a) and one week. But both experiments confirm that much of the polymer and crosslinker were stripped from solution by passing through 6 inches of 2-darcy rock.

From an extremely optimistic viewpoint, one could argue that some polymer and aluminum did propagate through the core. However, the major questions are: (a) how far would the polymer and/or crosslinker propagate into a real reservoir, and (b) given the immense level of stripping of polymer and aluminum from the solution, how would the resistance factor provided by the remaining polymer and aluminum (again, deep in the reservoir) compare to that for a normal polymer solution? Another question is

whether significant crosslinking will occur, given the low residual levels of polymer and aluminum remaining after flowing through 6-inches of porous rock.

Manrique et al. (2014) also stated that “Splido et al. (2009, 2010) demonstrated that CDG aged a few days could propagate through Berea cores”. A close look at Splido’s work reveals that their aged CDGs were “pre-generated nano-sized colloidal particles.” Fig. 2 of Splido et al. (2010) showed that the effluent polymer concentration reached 90–100% of the injected value, but the effluent aluminum reached only 35–40% of the injected value. Splido suggested that CDG with nanometer-sized CDG particles with a HPAM/aluminum ratio of 45:1 propagated through the Berea core, while the remaining aluminum (presumably that did not complex with the polymer) was retained by clays in the core. It is certainly conceivable that nanometer-sized particles would not be filtered out by moderate-to-high-permeability Berea sandstone. However, that still leaves the question as to whether that suspension would provide a resistance factor or residual resistance factor that was greater than that for Spildo’s 600-ppm HPAM formulation without aluminum. As mentioned earlier, Table 1 lists resistance and residual resistance factors for the three core sections of Spildo’s experiment. Presumably, the second section provides the most reliable results because it is longest and not subject to end effects. The second section shows a resistance factor of 5.8 and a residual resistance factor of 1.8. Spildo did not report what the values would be for a polymer solution (600-ppm) without the crosslinker. However, the values in the table below seem quite consistent with what would be expected from a 600-ppm HPAM solution. So, it is not at all obvious that the CDG provided more resistance factor or residual resistance factor than the polymer alone.

4. Field data claimed to support colloidal dispersion gels

One of the most persuasive arguments by vendors when selling CDGs to trusting customers are their claims that these treatments recover substantial amounts of oil in field applications. In this section, we focus on whether any of these field applications contradict the basic behavior observed in the laboratory—i.e., whether colloidal dispersion gels can propagate deep into the porous rock of a reservoir, and at the same time, provide resistance factors or residual resistance factors that are greater than those for the same polymer formulation without the crosslinker. If there is credible evidence, that might suggest that the laboratory experiments missed a critical aspect of how CDGs work. However, if no credible evidence is found, then whatever positive gains made by the field applications, the results could have been better if the operator had done things differently—e.g., by leaving out the crosslinker and just performing a well-designed polymer flood or by applying well-designed conventional gel treatments to plug fractures that caused channeling problems.

Fielding et al. (1994) described application of CDG (dilute Al-citrate-HPAM) and dilute Cr(III)-acetate-HPAM gel treatments in the North Rainbow Ranch Unit in Wyoming. The Minnelusa sandstone reservoir was located at 9500-ft depth, had temperature of 202 °F, porosity of 19.7%, and oil viscosity of 3.94 cp at reservoir temperature. Between 1973 and 1984, 17.2% OOIP was produced by

rock/fluid expansion during primary production, with no water production. Waterflooding started in 1984, and two water spikes occurred very shortly, followed by a rapid and sustained increase in water production about a year after starting the waterflood. Gels were injected only in one well: Carter 1–24A. A large volume of aluminum-citrate-HPAM CDG was injected (198000 bbl with 1200-ppm HPAM, followed by 654000 bbl with 300-ppm HPAM). Later 60000 bbl of Cr(III)-acetate-HPAM was injected with 1500-ppm HPAM. The paper stated “Natural fractures are not present in [the] reservoir.” That raises the question, if no fractures were present, how could the Al-citrate-HPAM gels be injected for several years and how could the Cr(III)-acetate-HPAM gel be injected for several weeks when the crosslinking or gelation time at 202 °F is less than 2 h? To be generous, four possibilities exist. First, after the gelation time, the gels might flow through the porous rock—like a super polymer flood. This is the scenario advocated by Fielding et al. as stated in their first three conclusions:

- “1. High molecular weight polymers (10MM + MW) can be successfully placed in non-fractured, high permeability sandstones.
2. Colloidal dispersion gel systems provide in-depth resistance to flow.
3. Bulk gel systems can be placed in non-fractured formations to provide in-depth drive fluid diversion.”

No evidence was provided at all to support these claims. Further, all credible published evidence disputes these claims. Concerning the first claim, there is no doubt that high-Mw polymers can flow into high-permeability rock. That is the basis of polymer flooding. However, the authors suggest that the polymer flows only into the most-permeable rock, but not less permeable rock. This implication was proven incorrect by Seright 1988, 1991a,b, Sorbie and Seright 1992, Seright et al., 1993, Liang et al., 1993, Seright and Liang 1994, 1995, Ye and Seright, 1996, Nimir and Seright 1996.

Further, there is NO credible evidence to support the second and third speculations above. Every credible laboratory study indicates that once gel particles have grown to approach the size of pore throats (which typically takes less than 2 h at 200 °F if the gelation reaction proceeds), they will not propagate through porous rock at any reasonable pressure gradient. (Of course, unreacted HPAM and crosslinker may propagate, but will not reduce mobility any more than the polymer without crosslinker.)

A second possibility is that fractures were actually open near the injector. The paper did not provide any information about the formation permeability, the reservoir pressure, the fluid level during water injection, or the viscosity of the gel formulations. They also did not provide any step-rate-test information. If we had this information, we could perform calculations to establish whether fractures intersected the injection well. Without the information or some other confirming information, there is no legitimate basis to claim that no fractures were present.

A third possibility is that the crosslinkers were stripped from the gelant formulations before gels could form, so only the polymer solution flowed through the porous rock.

A fourth possibility is that the polymer and gelant formulations degraded to low viscosity fluids during injection—which is quite possible considering the high temperature of 202 °F.

Mack and Smith (1997) described some of the typical philosophies toward colloidal dispersion gels that commonly were advocated by this vendor. An interesting statement was made in the abstract: “CDG’s should not be used in rock with extreme heterogeneity caused by fractures or extremely conductive channels.” We agree with this point. Gels like Cr(III)-acetate-HPAM with 0.5% or more HPAM are much more appropriate for treating channeling

Table 1
Resistance (RF) and residual resistance factors (RRF) for the three core sections.

Section	Length, cm	RF	RRF
1	2.5	4.0	4.0
2	15.8	5.8	1.8
3	11.0	8.3	3.0

through fractures.

Another statement in the introduction was: “Many technologies develop outside the realm of understanding, where the technology is developed and used before the science is fully understood. In-depth colloidal dispersion gels (CDG’s) fall into this category.” This would be a very open-minded statement if the CDG technology was new. But after 35 years with legitimate science and engineering consistently contradicting the vendor claims, it may be time to stop advocating CDGs. Normal polymer flooding and gel treatments to reduce channeling through fractures still require improvements to provide the best effect, but at least they are technologies with a credible science and engineering basis. Because of the invalid claims and concepts associated with CDG technology, those applying CDG floods may reach overly negative conclusions if they equate results from CDG floods to those from legitimate polymer floods.

Another statement was: “Field results suggest that the gels work by flooding preferred water flow paths between injectors and producers once-through, then restricting the flow paths to further water injection. This restriction in the high-permeability streaks in-depth forces subsequent water into tighter rock, thereby increasing sweep efficiency. The result is a more efficient flood than would be possible with straight water or even uncrosslinked mobility control polymer, in a heterogeneous reservoir.” There are no credible field comparisons that substantiate this claim. For this statement to be true, the CDG must be able to propagate deep into the porous rock of the reservoir and provide resistance factors and/or residual resistance factors that are greater than for polymer without crosslinker. The available evidence consistently demonstrates that does not happen.

As in many of their publications, the vendor advocates use of Hall plots. That would be ok except for the invalid conclusions that they draw from those plots. Because Hall plots only monitor injection pressures at the wellbore, they reflect the composite of face plugging/formation damage, in-situ mobility changes, and fracture extension. Hall plots cannot distinguish between these effects—so they cannot quantify in situ resistance factors or residual resistance factors. The authors state: “One explanation for the increase [in Hall plot slope] is that CDG blocked the most permeable flow paths, forcing the uncrosslinked polymer to move into lower permeability rock.” Because Hall plots cannot distinguish why pressures are increasing, this suggestion has the same validity as claiming that only the lower permeability rock was blocked—that is to say, it has no validity at all. Simple application of Darcy’s law (Seright, 1988) reveals that gelants will flow into all opens zones in proportion to their flow capacity. If a weak gel (like CDG) reduces the flow capacity of a high-permeability zone, it will also cause a significant reduction in flow capacity in less-permeable zones. In particular, if flow is radial, all open zones will experience proportionately about the same loss of productivity after a gelant flows into the rock and forms a gel (Seright, 1988).

Another point is that normal polymer floods improve vertical sweep efficiency when polymer solutions penetrate extensively into less-permeable zones (i.e., more than during a waterflood). The CDG vendor claims that CDG’s work as an improved polymer flood, but at the same time only penetrate into the most-permeable zone. So, their position holds two contradictory beliefs at the same time.

Concerning the paper’s conclusions:

Conclusion 1 was “CDG’s can be injected into consolidated, unfractured formations without near-wellbore plugging.” Nothing was presented at all in this paper to demonstrate that the injection wells did not intersect a fracture or that fractures were not extending during CDG injection. No step-rate tests were reported.

No calculations were made of injectivity index during injection of water, polymer, or CDG.

Conclusion 2 was “CDG’s cause resistance to flow in-depth and strongly affect subsurface water movement.” Part of this statement is based on Hall plots, which cannot distinguish in-depth mobility reduction from face plugging. Further, no evidence was presented that the CDG provided an “in-depth” effect that was greater than expectations for a polymer solution without the crosslinker.

Conclusion 3 was “Properly designed CDG’s stay in the reservoir.” If we ignore the term “properly designed”—well ..., yes, but they don’t penetrate deep into the porous rock of the reservoir and provide resistance factors and/or residual resistance factors that are greater than equivalent polymer solutions without the crosslinker.

Conclusion 4 was “When CDG’s are used in heterogeneous reservoirs, the result is a more efficient flood.” It is not any more efficient than a polymer flood without the crosslinker. Even if CDGs could propagate into the reservoir, the vendor should have injected larger volumes to improve the flood. The injected volumes are too small. For a credible polymer flood, they should have at least injected polymer until significant breakthrough occurred. All these CDG floods are “under-designed” even if the CDG could flow through porous rock.

Conclusion 5 was “The CDG process is field proven and results in higher recovery.” It is certainly not proven that the CDG flows deep into the porous rock of the reservoir. All indications are that it does not do this. Further, well-designed polymer floods would have performed better than the CDG floods.

Wouterlood et al. (2002) discussed applying Marcit treatments (using HPAM with ~14 million Dalton molecular weight and ~15% degree of hydrolysis—crosslinked with Cr(III) acetate). Marcit treatments were developed to treat channeling through fractures, and we strongly support their use for this purpose. The inventor of the Marcit technology, Robert Sydansk, consistently and exclusively advocated Marcit for fracture problems (Sydansk and Romero-Zeron, 2011). In contrast, the vendor advocates that crosslinked Marcit gels flow through porous rock. Since this paper may be part of the basis for the vendor’s belief that CDGs propagate deep into the porous rock of reservoirs, we will include a short review. Another key part of this paper is that “85% of the treatment volumes were in the range from 1500 to 2500 ppm” HPAM. The vast majority of other Marcit treatments that were sanctioned by the Marcit inventor contained at least 3000-ppm HPAM. For the 1500–2500 ppm formulations, gelant viscosity during injection was 15–25 cp.

Formation permeability was stated to range from 0.05 to 759 md. Oil viscosity was 1.5 cp. The waterflood mobility ratio was stated to be 1.4. Waterflooding started in 1975. At the time of the gel project (1999–2001), cumulative oil recovery was only 13.5% OOIP (after injecting ~1 PV of water), and producing water/oil ratios typically ranged from 2 to 20. The paper indicates that fractures did not play a significant role with channeling through this reservoir. However, solid evidence of this assumption was not presented. The presence of fractures seems quite likely considering the low water flood recovery factors, the high producing WOR ratios, and the stated waterflood mobility ratio was only 1.4. If flow was truly radial into unfractured injectors, the injectivity index while injecting the 15–25 cp gelant should have been less than 5% of that for water (Seright et al., 2009). The authors did not provide or compare injectivity indexes before or during the gel treatments.

The paper states: “The gelant preferentially seeks the most permeable water saturated zones, which can be either high permeability matrix or induced fractures.” Seright (2003) (and references therein) demonstrate that formed gels can extrude exclusively through fractures without entering the porous rock. However, if flow is radial into a reservoir with layers of different

permeability, basic Darcy-law calculations reveal that one must be concerned about damage the gelant causes when it enters and sets up on less-permeable hydrocarbon zones (Seright, 1988).

Concerning the paper's conclusions, we don't see evidence from this paper that fractures were not open at the wells during gelant injection. Instead, the low recovery factors and high WOR values (along with the low mobility ratio) indicates that fractures probably were open. We are concerned that Marcit gels with 1500–2500 ppm HPAM are not as effective as those with higher HPAM concentrations. However, they might provide some benefit in treating narrow fractures. We know that Cr(III)-HPAM gels that have undergone gelation do not flow through porous rock. Also, basic reservoir engineering (i.e., Darcy's law) should be respected. Without providing a specific scientific or engineering reason for justification, statements are nonsense if they claim that the gelant does not enter and cause substantial damage to oil-productive zones.

Chang et al. (2006) described a pilot project at Daqing where they injected 0.179 PV CDG, then 0.155 PV 600-ppm HPAM, then 0.196 PV CDG. The CDG formulation contained 600–700-ppm HPAM with 20–25-ppm Al (as citrate). The paper claimed that the CDG pilot recovered more oil (expressed as %OOIP) than “one of the best PF projects in Daqing”. This appears to be a self-serving statement that generates many unanswered questions. Perhaps, the chief question to ask is: If the CDG process was so much more effective than polymer flooding, why did Daqing not substitute CDGs for polymer flooding during their subsequent development of the field? (Wang et al., 2008a,b).

Fig. 5 from the paper plotted injection pressure versus time during CDG and polymer injection. Fig. 6 of the paper shows a Hall plot generated from this data. A key point to note is that during injection of 20-cp CDG/polymer solutions the injectivity index only dropped by ~35–40%, compared with water injection. This indicates that fractures were open during polymer injection. If this were not true (i.e., if flow were radial around the injectors), the injectivity index should have dropped by more than 90% (Wang et al., 2008a; Seright et al., 2009; Manichand et al., 2013).

Chang et al. stated: “According to the slopes in the Hall plot ..., as shown in Fig. 6, the resistance factor in the reservoir was low at the beginning of CDG injection and increased gradually as more CDG slug was injected. The resistance factor decreased during the polymer injection and then increased again in the second CDG injection, indicating that the CDG solution formed strong resistance deep in the reservoir and did not create any plugging effects in the near-wellbore region. The sustained high resistance factor after CDG injection demonstrated that the residual resistance factor created by the CDG system is higher than the PF.” The key point here is that Hall plots cannot be used to judge what is happening deep in the reservoir. The input pressure for the Hall plot is strictly the injection pressure. Any increases or decreases in the injection pressure (and the Hall plot slope) reflect the composite of in-situ mobility changes, face plugging at the injection sand face, and fracture extension. Hall plots cannot determine resistance factors or residual resistance factors deep in the reservoir. So, Chang's statement is not valid.

Concerning “Volumetric Sweep”, Chang et al. stated: “Results of the profile improvements from prechemical injection through the entire chemical-injection period (Table 11 of the paper) show that, indeed, the injection profiles were improved and injection fluids were diverted from high-permeability zones into medium- and low-permeability zones in all wells at different degrees after injection of the CDG solution.” It is not at all surprising that injection of a 20-cp polymer formulation should improve the injection profile. This is basic fluid mechanics and can be viewed in videos at: <http://baervan.nmt.edu/groups/res-sweep/>. A second point is that

close examination of their Table 11 does not indicate that the CDG formulation improved the injection profile any better than the polymer solution without the crosslinker. This result is also expected since both formulations were indicated to have viscosities around 20 cp. (As with many field results, Table 11 showed significant variation in results from one well and time period to the next.) A third point to keep in mind is that the CDG and polymer formulations were probably injected above the formation parting pressure (because the CDG/polymer injectivity index was only 35–40% less than that for water injection). If near-wellbore fractures are open, injection profiles have diminished value because fluids can crossflow up or down the fracture after they leave the wellbore. Chang et al. ultimately concludes (in their Conclusion 3): “The pilot test proved that the CDG system could be used more effectively than PF to adjust the permeability variations and improve the volumetric sweep in heterogeneous reservoirs.” Apparently, this conclusion was based entirely on slight modifications of Hall plots in Fig. 6. As we pointed out during our discussion of Fig. 6, Hall plots cannot be used to assess what happens beyond the injection wellbore, because they reflect a composite of in-situ mobility changes, face plugging at the injection sand face, and fracture extension. Hall plots cannot prove “that the CDG system could be used more effectively than PF to adjust the permeability variations and improve the volumetric sweep in heterogeneous reservoirs.”

A positive feature of Chang's study was that they monitored polymer and aluminum concentrations in the produced fluids. After the project switched from injecting polymer solution (without crosslinker) to the second CDG bank, Chang noted that the produced polymer concentration in the central production well dropped from 326 to 156 mg/L. Chang interpreted this to mean: “These results show that the second CDG slug after polymer injection can continue to improve the injection profile and volumetric sweep although the effectiveness is not as high as that of the first CDG slug.” Chang continued by saying “The aluminum concentration remained at a very low level, in the range from 1 to 5 mg/L. The detection of aluminum ions in the central producer is evidence of proper transporting of the crosslinker as well as the polymer through the reservoir.” This seems to be an odd conclusion when 80% to almost 100% of the aluminum was stripped from the formulation. A more viable interpretation is that the drop in polymer concentration (from 326 to 156 mg/L) was due to stripping of virtually all of the crosslinked polymer (i.e., the CDG particles that were larger than pore throats) near the injection wellbore [or more specifically within 15 days (or much less) of entering the porous rock]. We presume that the polymer that was not crosslinked continued to propagate through the formation and provide some mobility reduction. However, 156-mg/L of uncrosslinked polymer will provide less mobility reduction than 326 mg/L of polymer.

The main conclusion of the paper that appears invalid is Conclusion 3: “The pilot test proved that the CDG system could be used more effectively than PF to adjust the permeability variations and improve the volumetric sweep in heterogeneous reservoirs.” This conclusion was based entirely on slight modifications of Hall plots in Fig. 6 and is false, as discussed above.

At the end of this paper, an important question to ask is: If the CDG process was so much more effective than polymer flooding, why did Daqing not substitute CDGs for polymer flooding during their subsequent development of the field? Views opposing that of Chang et al. concerning CDGs at Daqing can be found in Wang et al. (2008a) and in Seright et al. (2006).

Norman et al. (2006) discussed applying Marcit treatments (using 4000–7000 ppm of HPAM with 8–13 million Dalton molecular weight and 8–15% degree of hydrolysis—crosslinked with Cr(III) acetate). Marcit treatments were developed to treat

channeling through fractures, and we strongly support their use for this purpose. The general field description of the paper is good. A particularly positive aspect of the paper is their use of tracers before and after gel treatments.

The first controversial statement in the paper is: “In order to avoid viscosity loss and polymer degradation, a metal ion cross-linker such as Cr^{3+} can be introduced which attaches to the anionic site of the polyacrylamide.” The authors appear to believe that gels are simply more viscous versions of polymer solutions. The central problem with this idea is that the crosslinked polymer particles (i.e., gels) that are larger than pore throats will not propagate through porous media.

The authors cite results of 50 bullheaded gel treatments “that did not indicate linear flow had been completed with no post treatment injectivity loss in lower permeability zones.” We acknowledge that Cr(III)-acetate-HPAM gels (i.e., fluid uncrosslinked polymer formulations before the gelation time) can readily flow into porous rock. However, after the gelation time (which is less than 2 h at the author’s reservoir temperature of 98 °C), the gel will not flow through porous rock (Sydansk and Romero-Zeron, 2011). The logical way to rationalize these observations is that near wellbore fractures were open in the wells that allowed the gels to be injected. Because of these fractures, injection profiles were of little value in judging conformance improvement.

A second controversial statement was: “Gelant subjected to higher shear rates forms weaker gels than gelant subjected to lower shear rates. Equation (1) shows that low permeability rocks (that generally correspond to lower porosities and lower water saturations) will impart a higher shear rate on the injected polymer gel solution. Thus, the gelant forms weaker gels in the lower permeability zones that result in lower residual resistance factors and maintained injectivity.”

$$\gamma_c = 2\mu / (2 k_p S_w \phi)^{0.5} \quad (1)$$

There are two major problems with this logic. The first is that it incorrectly assumes that fluid velocities are the same in high and low permeability zones. As an example, consider two zones, one with 1000 md and the other with 100 md. If the injected fluid had a viscosity of 1 cp, the velocity in the 1000 md layer would be 10 times greater than in the 100 md layer—making the shear rate $((10/\sqrt{1000})/(1/\sqrt{100})) = 3.16$ times higher in the high permeability layer. Of course, this finding is in direct contradiction to the author’s statement. In truth, when injecting viscous gelants (like a 20-cp Marcit fluid before gelation), Seright (1988) demonstrated that the fluid velocity in a 1000 md layer would only be $\sqrt{1000/100}$ or 3.16 times higher than in the 100 md layer—making the shear rate $[(3.16/\sqrt{1000})/(1/\sqrt{100}) = 1] = 1$ or the same in the two layers. Again, this contradicts the statement by Norman et al. The second major problem with their statement is that experimental results with polymers, particulates, weak gels, and colloidal dispersion gels have consistently demonstrated that resistance factors and residual resistance factors are at least as great in low permeability rock as in high permeability rock. Not surprisingly, particles (including gel particles) plug or reduce the flow capacity of small pores at least as much as large pores. Examples can be found in (Pye, 1964; Jennings et al., 1971; Hirasaki and Pope, 1974; Vela et al., 1976; Jewett and Schurz, 1970; Duda et al., 1983; Zaitoun and Kohler, 1987; Rousseau et al., 2005), among others. Smith et al. (2000) applies specifically to Al-citrate-HPAM colloidal dispersion gels and was written by Julie Smith, who was a co-worker with the first author Norman et al. (2006). So it seems odd that Norman et al. would make this contradictory claim.

As mentioned earlier, a positive aspect of this work was tracer

studies before and after gel injection. It is interesting that the peak in the tracer responses typically ranged from 100 to 250 days. Usually, we don’t associate severe channeling through fractures with inter-well tracer times that are this long.

The paper was critical of our previous use of Eq. (2) below as a means to diagnose problems with channeling through fractures (Seright et al., 2003). We agree with the principle conclusion by the authors that application of Eq. (2) did not suggest that fractures caused severe channeling in the work of Norman et al. (2006). However, the paper concluded that flow around the injection wellbores was radial based on the calculations—i.e., that no fractures were present. This conclusion is not correct. Our use of Eq. (2) advocated that if the left side of Eq. (2) was 5X greater than the right side—that provides definitive evidence of a fracture in the injector (Seright et al., 2003). If the left side was less than 5X greater than the right side, a fracture could still be present. That fracture could still allow extensive injection of a Cr(III)-acetate-HPAM gel, because the gel extrudes through the open fracture and the fracture extends with increased gel injection (Seright, 2003; Seright et al., 2009).

$$q/\Delta P = \sum kh / [141.2 \mu \ln(r_e/r_w)] \quad (2)$$

Extensive studies have proven that formed Cr(III)-acetate-HPAM gels cannot/do not flow through porous rock (Seright, 2003 and references therein). Consequently, the only viable conclusion in this work was that fractures were open near wellbore to allow gel injection. Again, these fractures probably did not cause severe channeling through the reservoir (as evidenced by the inter-well tracer results in Norman et al.). We support use of Marcit gel treatments to reduce channeling through fractures. There are many definitive field cases of these applications (see Sydansk and Southwell, 2000; Hild and Wackowski, 1999; Borling, 1994).

The only conclusion that we don’t accept in this paper is Conclusion 3: “Zone isolation during a polymer gel treatment is not necessarily required in matrix reservoirs where heterogeneity has been documented by injection profiles, tracers and/or production history.” The statement could be true under some circumstances (as in Plahn et al., 1998), but not for the reasons advocated by Norman et al. (2006). The most viable explanation for the acceptable injectivity for gels in this paper is that near wellbore fractures were open.

Diaz et al. (2008, 2015) describes a field application (Loma Alta Sur field in Argentina) where 300–600-ppm HPAM solutions were injected along with Cr(III) acetate. Total pay was 35 m, Dykstra-Parsons permeability variation was 0.89, and oil viscosity was 30 cp at the reservoir temperature of 45 °C. The authors presented convincing inter-well tracer evidence that fractures did not cause significant channeling between wells. Overall, this field appears to be a good candidate for polymer flooding.

The papers contain a mixed discussion of the effects of shear and the necessity for zone isolation. A statement that offers middle ground on the CDG controversy was “Sydansk (2006, 2007) postulates that most, if not all reservoirs characterized as matrix rock are in fact fractured due to injection above fracture pressure, undetected micro-fractures and/or extremely high permeability anomalies that exhibit fracture like behavior. Such reservoir heterogeneities, difficult to quantify at a macroscopic level, offer a credible hypothesis for the mechanism of colloidal dispersion gel propagation in a reservoir.”

The papers present an overly optimistic projection of the impact of the CDG application. A very pessimistic “waterflood oil trend” was chosen to justify incremental oil from the CDG application. Examination of their data reveals that an alternative waterflood oil trend could have been chosen that indicated no incremental oil. We

don't take a position about whether this project did/did not recover incremental oil. It is quite conceivable to us that polymer moving without the crosslinker may have provided some benefit. However, we don't see definitive evidence that the CDG provided any benefit above that provided by the polymer without the crosslinker. The papers state that no polymer was detected in offset production wells. No information was offered about whether crosslinker was monitored in the production wells.

We don't disagree with any of the conclusions of the papers. We simply contend that the CDG did not add anything to the project that would not have been added by injecting equivalent polymer solutions with no crosslinker.

Muruaga et al. (2008) described a field application (El Tordillo field in Argentina) where 18% PV CDG is applied after application of Marcit gel treatments. The Marcit gel treatments were stated as being directed at reducing channeling through fractures. We applaud and support the Marcit portion of the work. A particularly positive aspect was performing inter-well tracer studies before and after application of the Marcit treatments. In one case, inter-well tracer transit time increased from ~10 h before the Marcit treatment to ~700 h after the treatment—providing a clear indication of the success of the treatment.

The controversy comes from the CDG portion: “CDG's are typically large volume, low polymer concentration gels designed to improve sweep efficiency in unfractured matrix reservoirs that exhibit poor waterflood performance.” On the one hand, the reservoir had a significant permeability variation within the porous rock (Dykstra-Parsons coefficient of 0.8; median permeability of 175 md) and an oil viscosity of 28 cp at the reservoir temperature of 85 °C. These factors suggest that the reservoir is quite reasonably a candidate for polymer flooding. If the crosslinker (Cr or Al) is stripped from the CDG formulation, free-flowing polymer solution can provide conformance/sweep improvement in this reservoir. The central controversy is whether the crosslinker and/or crosslinked polymer (i.e., the CDG) will propagate any significant distance into the porous rock. If the answer is “no”, then the money spent on the CDG crosslinker was wasted, and the effective portion of the polymer flood (i.e., the HPAM concentration) may have been under-designed.

CDG of unspecified composition was injected into two wells for 10 months. The reservoir temperature was 85 °C, the median rock permeability was 175 md, and the oil viscosity at reservoir temperature was 28 cp. An interesting statement was “During the course of the project, the crosslinker was briefly suspended in order to maintain the injection pressure below formation parting pressure. On each occasion, the injection pressure immediately stabilized and began to slowly decline, confirming that a chemical reaction was in fact occurring between the polymer and crosslinking agent (i.e., gel formation).” We don't disagree with this statement. However, the paper goes on to say: “Some researchers have used simplistic multi-layer models and homogeneous cores to simulate gel placement in unfractured reservoirs, with the implicit assumption that permeability and fluid saturations in each layer are uniform (Seright, 1988; Sorbie and Seright, 1992). Core samples are typically one inch in diameter, three inches long, and homogeneous. As noted by Christiansen (2001), extrapolating results from core samples to a reservoir scale is “an unresolved topic of current investigation by engineers around the world.” The message from Muruaga et al. (2008) appears to be that the CDG process is too complicated to understand, so therefore it works. In contrast, our contention is that once the crosslinking reaction occurs (e.g., within about 1 day after injection), crosslinked polymer (i.e., gel aggregates that are larger than pore throats) no longer flows through porous rock. Any uncrosslinked polymer is free to flow through the porous rock and provide the benefits of a polymer flood. However,

the crosslinker served no useful purpose in the polymer-flood portion of the project. (We do agree that the previous Marcit treatments, with high polymer and crosslinker concentrations, were very effective in reducing flow through the fractures.)

Another interesting statement was: “All offset producing wells were tested for polymer breakthrough several times a week. There was no polymer detected at any of the producing wells during the course of the CDG treatments.” This finding is quite reasonable and confirms the effectiveness of the previous Marcit gel treatments in reducing channeling through fractures. It is also consistent with injecting only 18% PV polymer/CDG bank. However, it seems odd that they did not monitor crosslinker (either Al or Cr) in the production wells. If the vendor wanted to prove that CDGs propagate intact through the reservoir rock, detection of Al or Cr would have been an effective method to make that point.

Another statement was: “The operator did not experience any difficulties injecting water in any of the layers following the CDG treatments, confirming that the CDG's did not “plug” the lower permeability reservoir rock.” Table 2 of the paper provides some interesting insights. First, the water injection rate after the CDG (237.5 m³/day) was greater than before the CDG application (229.5 m³/day). If the CDG had a significant viscosity (e.g., more than 2X that of water), the injectivity index should have decreased if no fractures were open. The results suggest that a fracture was open near the wellbore. This result would be expected since pressures are greatest near the injection well. Farther from the well, pressures decrease—allowing fractures to close if obstructions (e.g., proppant) are not present. The suggestion of an open fracture helps explain the results in Table 2 of the paper. The most-permeable (CR28-40) and fourth-most permeable (CR29-30) layers apparently decreased in flow capacity, while the second-most-permeable (CR29-50), third-most-permeable (CR28-30), and the least-permeable (CR28-20) apparently increased in flow capacity. If no fracture was open near the wellbore, it would be difficult to explain this result without resorting to black magic.

In contrast, a viable explanation is available if a fracture was open near the injection well. That is, flow enters different vertical portions of the fracture as governed by local restrictions/anomalies present in the wellbore and at the fracture entry. This provides the flow distribution observed/reported in the paper. Thereafter, the fluid re-distributes up/down within the fracture to satisfy the actual flow capacities of the rock (governed by Darcy's law). Since the profiling tool cannot detect flow beyond the wellbore, it cannot determine the actual layer-by-layer flow distribution. In other words, the flow profiles in the table above (and other parts of the paper) may be meaningless.

We don't disagree with any of the conclusions of the paper. We simply contend that the CDG did not add anything to the project that would not have been added by injecting equivalent polymer solutions with no crosslinker.

Guo et al. (2011) claim that basically different mechanisms of oil recovery exist between polymer flooding and CDG flooding. The abstract states: “The injection capacity of the two processes are about the same, but polymer flooding features large injection increase amplitude, quick pressure increase in initial period and quick decrease for subsequent flooding pressure; while CDG injection features a slower and gradual increase and decrease. The oil recovery effect for polymer flooding is mainly realized during the process of polymer injection, featuring quick water cut decrease and fairly quick increase as well quick water cut increase for subsequent water flooding; the oil displacement effect of CDG is equivalent of that for polymer flooding during chemical injection, but performs much better than polymer during subsequent water flooding.” A detailed examination of the paper reveals that the above claims are unsupported and overly optimistic.

The paper compares polymer flooding versus CDG flooding in the Duanxi of B1 area of the Daqing oilfield. The paper states: “The polymer flood was conducted for the P11–4 formations. The start date was January 8, 1993 and ended on October 10, 1998 when the water-cut of producers reached 97.2%, with a duration of the project for 69 months; the CDG profile modification pilot was conducted in the SA II1-2 formation. The starting date was May 1999 and the project ended in October 2008 with water-cut of 96.1% with the duration of the project for 112 months.” The polymer flooded area was about twice as thick and about 30% more permeable than the CDG flooded area. Compared with the polymer flooded area, the CDG area was about four times as large, involved four times as many injectors, three times as many producers, and eight times as many “central wells”. For the polymer flood, the average injection rate was 2.5 times higher than the CDG flood, the polymer concentration was 791-ppm (versus 600-ppm for the CDG flood), and the amount of chemical injected (in mg/L-PV) was about 25% less for the polymer flood than for the CDG flood.

The paper states that produced polymer concentrations peaked at 600–800 mg/l in the polymer flooded area. It also states: “As for the CDG profile modification case, the polymer production was very low throughout the entire injection of the first CDG slug. However, after the termination of the first CDG slug, the produced polymer concentration increased significantly, from ~34 mg/l to ~400 mg/l within 3 months of the polymer injection. During the second CDG slug injection, produced polymer concentration decreased again to ~110 mg/l. After the pilot area was converted to water injection, the produced polymer concentration started to increase to a peak of ~470 mg/l and then decreased gradually. The production of polymer in production wells continued throughout the pilot at ~250 mg/l” These observations suggest that significant levels of crosslinked polymer (i.e., CDG) were stripped from the solution as it propagated into the formation. It would have been interesting to monitor the aluminum content in the produced fluids.

In Section 2 of the paper (the field data), the presentation was reasonably factual. However, the discussion part of this paper (Section 3) leaps to several invalid conclusions. First, concerning injectivity: “In the initial period of injection, the increase in oil recovery in the polymer process was significant and it has a much higher increase in pressure than the CDG case, indicating that CDG has higher injection capacity than that of the polymer process. These results are similar to core flood experiments.” In truth, several factors influence injectivity here: (1) the polymer solution was more viscous than the CDG (because the CDG contained 24% less polymer), (2) the CDG formulation may have contained some crosslinked polymer that would form a filter cake, and (3) near-wellbore fractures have a large impact on injectivity and those fractures are often different from one well to the next. The viscosity of the injected fluids was apparently around 22 cp for the polymer solution and at least 10 cp for the CDG (these are guesses based on the stated polymer concentrations). If no fractures were present, injectivities should have decreased far more than reported in the paper. Further, near-wellbore fractures are known to be common at Daqing (Wang et al., 2008a). Therefore, it seems likely that well-to-well differences in near-wellbore fractures were the primary cause of differences in injectivity that were observed.

Second, concerning profile modification, the paper states “Polymer also has the ability to provide a certain degree of profile modification but the effectiveness is much lower than CDG,” A table with four listings was provided (apparently, two with polymer injection and two with CDG injection in the same well?). Three of the four listings appeared very similar—which raises doubts how they concluded that CDG was better. Most of their other arguments about profile improvement focused on reductions of injectivity and water cut. However, in view of doubts about the ability of CDG to

propagate deep into the reservoir, it seems more likely that these differences occurred primarily because of other well-to-well and pattern-to-pattern differences and variations.

The paper also states: “the residual resistance factor for polymer flood is much lower than the CDG flood.” Their logic was that (1) less polymer was produced from the CDG patterns than the polymer patterns, and (2) therefore, CDG retention was higher than polymer retention, and (3) therefore the residual resistance factor was higher for CDG than for polymer. The flaw with this logic revolves around where in the formation that the CDG retention occurred. If it occurred soon after it entered the porous rock, then the desired mobility reduction was not available to aid oil displacement deep in the reservoir. Their argument would have been much stronger if they had observed significant aluminum concentration in the produced fluids.

Third, concerning sweep improvement, the paper states “The CDG slug enters preferentially into the high permeability formation first and developing a substantial resistance which then cause the pressure increase in injection wells. The initial fluid distribution was 13.4% and 86.6% for low and high permeability strata, respectively. As the resistance increases continuously in the high permeability formation, more fluid was diverted into the medium and low permeability formation with the distribution of 39.2% and 60.8%.” This argument violates Darcy’s law. Unless there is a known reason for doing otherwise, fluids enter all zones at the same time in accordance with Darcy’s law, as shown in Seright (1988) and in the videos at www.prrc.nmt.edu/randey. As mentioned in the laboratory section above, Smith et al. (2000) reported that CDG residual resistance factors were found to range from 28 to 37 for CDG in a ~3000-md core and from 55 to 63 in a ~1000-md core. We also note that one of the two polymer-flood injection profiles (listed in Table 7 of the paper) showed basically the same values as for the two CDG cases. So the authors were pretty selective in choosing data to prove their point. It seems more likely that the profiles were basically meaningless—because near-wellbore fractures were open (as mentioned above) and fluids could re-distribute in the fracture in an undetectable way after they left the wellbore.

The paper also argues that CDG extended oil production and reduced water production for a longer period than polymer flooding. The paper stated “Most of increase oil recovery in the CDG process was from the water drive stage.” This statement appears to violate basic fluid mechanics, as demonstrated during the water injection phase of the videos at www.prrc.nmt.edu/randey. During water injection with either CDG or polymer flooding, the injected water will quickly form viscous fingers through the most-permeable zone. It seems more likely that whatever differences noted in the paper (for CDG versus polymer flooding) were due to the many differences in timing, location, well, and reservoir properties between the two floods.

For the reasons mentioned above, none of the first five conclusions of the paper are valid. The following conclusion was particularly controversial: “The profile modification performance by CDG is better than that of the polymer. The CDG solution can flow through the porous media in the reservoir and reach deeply into the formation, providing the effect of in-depth profile modification. Its blocking effect in the high permeability formation is higher than that of the polymer with higher polymer retention and slow polymer production in the production well. The effect of profile modification not only is effective in the CDG injection stage but even more pronounced in the subsequent water drive.”

If CDGs are so much better than polymer flooding, why did Daqing not implement large-scale CDG floods instead of polymer flooding?

Castro et al. (2013) described the design and implementation of a 1-injector, 3-producer CDG pilot project in the Dina Cretaceous

field in Colombia, where 437,000 bbl of CDG (5% PV) were injected. In this field project, the CDG contained 400-ppm HPAM and from 5 to 10-ppm aluminum. Water was injected into the reservoir since 1985, resulting in a recovery factor of 32% and water cuts of 96% at the time of the CDG project. Permeability ranged from 50 to 200 md, and reservoir temperature was 152 °F (67 °C). The waterflood mobility ratio was stated to be > 4 . Oil viscosity at reservoir conditions was 10–12 cp. This information suggests a reasonable candidate for polymer flooding.

The paper described a simulation effort that assumed that CDGs are simply viscous polymer solutions (that provide 10–60 cp viscosity) that provide greater residual resistance factors (3–10) than polymer solutions. If these assumptions were correct, we don't doubt the outcome provided by the simulator. However, we don't believe that the input viscosities and residual resistance factors for the CDG are credible.

We don't have any comment on the field results and conclusions from this paper, except to note that polymer solutions (with the same polymer concentration as in the CDG formulation) with no crosslinker would have performed at least as well as the CDG.

Manrique et al. (2014) examined 31 CDG floods. The authors attempted to argue that the CDG propagates through porous media and provides mobility reduction better than that for polymer without crosslinker. However, their own data reveals that they are not correct. To demonstrate that CDGs do propagate, you should be able to collect fluids at a production well and measure significant polymer and aluminum concentrations and show that those fluids have some viscosity or can provide mobility reduction. The abstract of the paper states “Despite large volumes of CDG injected production of polymer in offset producers has rarely been detected.” Although they do not say it, we assume that they have never detected the crosslinker in production wells either.

Some curious statements were made in the paper's introduction. In particular, the paper states: “However, despite numerous successful field results reported in the literature, laboratory-scale experiments (Al-Assi et al., 2009; Ranganathan et al., 1998; Seright 1994, 2013, 2013) have generated controversy regarding the ability to inject CDG's in large volumes without reducing injectivity while also improving sweep efficiency.” Actually, we have little doubt that CDGs, polymer solutions, and particulate suspensions can and have been injected into many formations with little reduction in injectivity. But this occurs because of fracture extension—not because of any magic property associated with the injected formulation. The real controversy is whether crosslinked polymers (specifically CDGs) can propagate deep into the porous rock of a reservoir, and at the same time, provide resistance factors or residual resistance factors that are greater than those for the same polymer formulation without the crosslinker.

Manrique et al. (2014) state that “None of the projects showed prolonged continuous increase in injection pressures.” Many normal polymer floods experienced a similar behavior. If a formulation is injected that is more viscous/less mobile than water, this observation suggests that the wells may be fractured. As more viscous fluid is injected, fractures simply extend to accommodate the injected viscous fluid (see Seright et al., 2009; Manichand et al., 2013). Although operators commonly define a “fracture pressure” or a pressure that they agree they will not exceed during the project, the true pressure at which fractures will be open and will extend is very often below this pre-selected value.

We applaud the use of Marcit gels before application of the CDG or polymer to prevent channeling of the “mobility control” fluids through fractures. Fig. 3 of Manrique et al. (2014) was claimed to “clearly suggest that CDG (after Marcit treatments) could be injected without face plugging as reported in some laboratory studies”. However, simple application of Marcit treatments does

not guarantee that the fractures are completely healed. Marcit gels are very useful in reducing the degree of channeling through fractures, but their soft, compliant nature allows fractures to reopen if the pressure increases enough to push the rock apart. Consequently, the authors are incorrect in suggesting that this data provides “useful information regarding possible gel formation and its propagation through the porous media.”

Manrique et al. (2014) discussed the use of Hall plots during applications of Marcit treatments and CDG floods. We don't disagree with many of the observations presented. However, for reasons mentioned above, we seriously doubt that these projects injected CDG with fractures not open. Fig. 6 from the paper shows Hall plots from three CDG floods and three polymer floods. All six plots were fairly linear—meaning that if the injection rates were constant, the wellhead pressures were also fairly constant. If a viscous fluid was injected into an unfractured reservoir after an extensive waterflood, Darcy's law requires that the wellhead pressure should increase. The fact that it did not means either (1) the polymer or CDG completely degraded upon injection or (2) fractures were present that extended to accommodate the injected fluid (this is the more likely possibility). Consequently, the Hall plots do not provide “evidence that CDG can be formed and propagated in the reservoir” or that CDGs propagate “through the reservoir despite some laboratory studies concluding the opposite.”

Manrique et al. (2014) also offered a figure as evidence that “strongly suggest that co-injected polymer and crosslinker do react in the reservoir” and “a good example of CDG formation and its propagation in a low permeability reservoir”. They state “five months after the second phase of CDG injection was completed, injection rates were decreased (700 bbl/d) due to the increase of wellhead injection pressures caused by water diversion to lower permeability intervals and continued water injection below the parting pressure. Injectivity reduction should be expected due to water diversion into low flow-capacity (unswept) zones. A sharper increase in positive skin (Trend II in Fig. 9) and no polymer production in offset producers suggest that in-depth permeability reduction occurred.”

The paper includes a summary of a simulation effort. It appears that effort assumed that CDGs simply act like polymer solutions—in that they propagated through the reservoir and provided some level of mobility reduction. Unfortunately, the central problem is that there is no credible evidence that CDGs (1) propagate through the reservoir and (2) at the same time provide a resistance factor or residual resistance factor that is greater than that for the polymer solutions without the crosslinker. Consequently, the CDG assumptions in the simulation effort are seriously flawed.

Several of the conclusions from the paper are not valid:

Conclusion 1—“Injection logs, well injectivity, and Hall plots confirm that CDG's do not significantly reduce injectivity and can propagate in the reservoir.” The reason that the CDGs did not reduce injectivity was probably because of fracture extension. If this were not true, injectivity should have gone down during injection of a fluid with a mobility that was lower than that of water. The claim that the CDGs propagate in the reservoir has no legitimate basis. To demonstrate that CDGs do propagate, fluids should be collected at a production well and reveal significant polymer and aluminum concentrations. Those fluids should have some viscosity or provide mobility reduction. The abstract of the paper states “Despite large volumes of CDG injected production of polymer in offset producers has rarely been detected.” Although they do not say it, we assume that they never detected crosslinker in production wells either.

Conclusion 2—“... large volumes of CDG can be injected below maximum pressure operating conditions (i.e., below the fracture

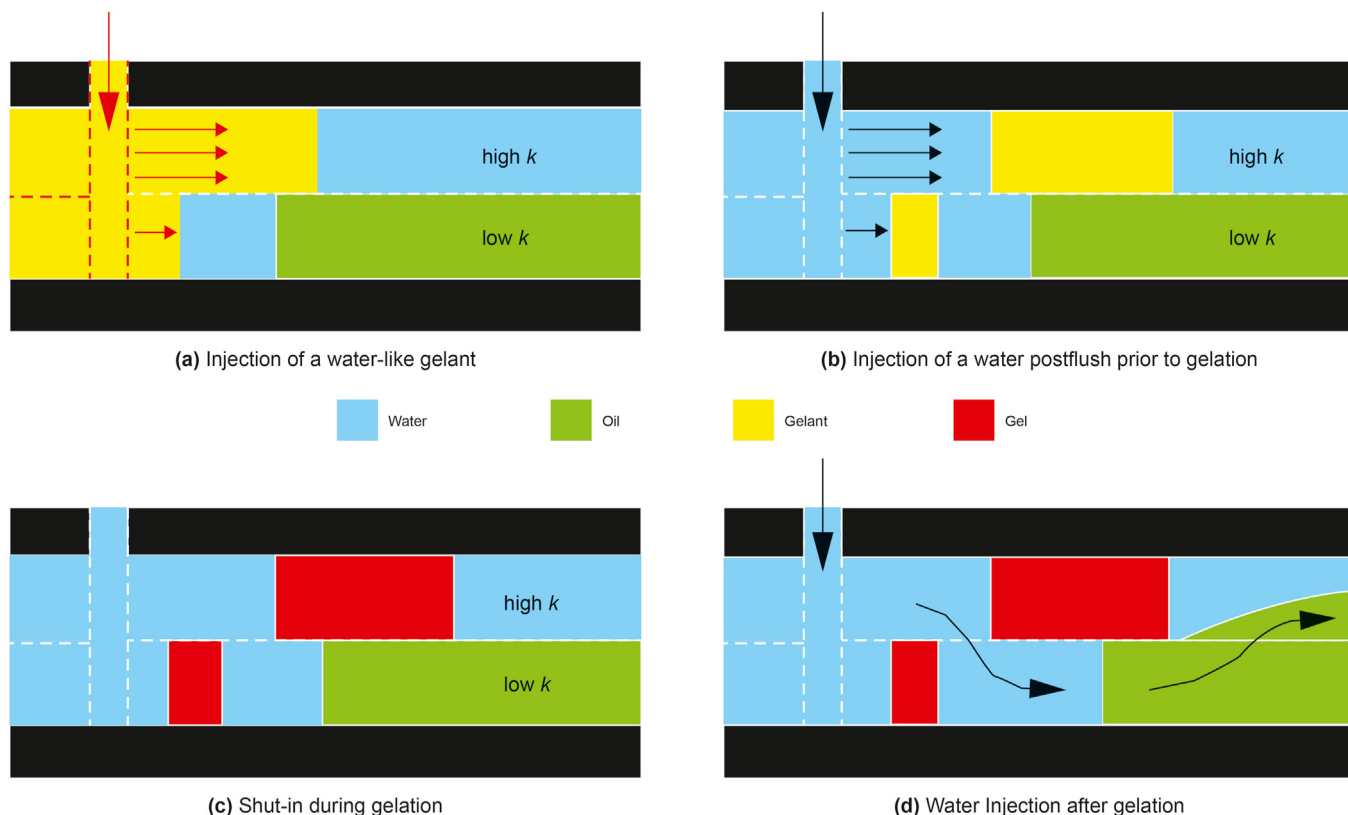


Fig. 1. In-depth profile control.

gradient ...". For the reasons mentioned above, it seems likely that fractures were open during CDG injection.

Conclusion 4—"Simulation results indicate that polymer flooding and CDG flooding may produce similar final oil recovery but polymer flooding will require more polymer mass." This conclusion assumes that CDGs can propagate deep into the porous rock of a reservoir and provide mobility reductions that are greater than for the polymer formulation without crosslinker. There is no credible evidence to support this position.

Conclusion 5—"The Hall plot represents a good diagnostic tool for performance evaluation of conformance or mobility control methods including CDG. It gives solid indications of permeability, skin effects, and changes in drainage area (i.e., flow diversion) supporting project interpretation." Hall plots only indicate pressures at the injection well. Consequently, they cannot, by themselves, indicate conformance, mobility control, or flow diversion.

Han et al. (2014) reviewed "in-depth fluid diversion technology", including CDGs, but their analysis was not particularly critical or analytical about the reported results. No insights were provided that impacted our central question: whether colloidal dispersion gels can propagate deep into the porous rock of a reservoir, and at the same time, provide resistance factors or residual resistance factors that are greater than those for the same polymer formulation without the crosslinker.

Leon et al. (2018) presented "Use of Cross-Linked Polymer Systems to Improve Volumetric Sweep Efficiency and Alternative Full Field Development Strategy for a Mature Waterflooding Optimization Processes - Dina Cretaceous Field Case", including CDGs. The results of a CDG pilot test in four wells was presented, and the steps taken toward the field expansion and CDG injection in 11 patterns were discussed. The author claimed: (1) the main advantages of microgels over polymer injection are that microgels can achieve

higher viscosities with low polymer concentrations, and generate higher residual resistance factors (RRF), (2) microgels have greater operational flexibility and injectivity than a conventional polymer injection as they are injected at low concentration and low viscosities and their generation occurs at the reservoir. No evidence was provided to support the first claim. For the second claim, even better operational flexibility and injectivity would have been realized if they had injected the same polymer concentration without the crosslinker. In this project, the CDG formulation was injected after polymer (400–1000 ppm) injection or water injection. Their presentation did not allow distinction in field performance between injection of polymer versus the CDG formulation.

Lobanova et al. (2020) applied cyclic gel-polymer flooding in the Buzachi North field in Kazakhstan. They employed three processes: (1) "strong" gels to plug fractures and fracture-like features first, (2) followed by "profile log alignment", and (3) finally, polymer flooding. We agree with and support this approach except for a critical detail in their "polymer flood". The oil viscosity was 316–417 cp, and the operator targeted 40-100-cp polymer solutions to improve the mobility ratio. However, achieving their desired injection viscosity required 3000-ppm HPAM under their conditions. So, the operator chose to add an aluminum-citrate crosslinker, which they claimed could achieve the desired viscosity with more than a twofold reduction of the HPAM concentration. Unfortunately, they provided no evidence that this formulation (after crosslinking) could flow through porous rock and at the same time, provide a resistance factor or residual resistance factor great than that without the crosslinker. Field results were presented where a notable decrease in water cut and an increase in oil rate were observed immediately after application of their "strong" gel treatments. We interpret this result as the immediate response to plugging fractures and fracture-like features using the "strong" gel

treatments. After this fast response, the water cut continued to follow the same increasing trend that was observed before the strong gel treatments. It seems likely that some benefit occurred from the subsequent “polymer flood”, but we see no reason to believe that the aluminum citrate crosslinker provided any benefit. It is understandable that the operator desired a less expensive process than using 3000-ppm HPAM. A better choice in this case would have been to inject the 1000+–ppm HPAM solution with no crosslinker. That process would not provide as great of improvement in mobility ratio (as when using 3000-ppm HPAM), but the improvement would still be significant (i.e., much better than a waterflood). Finally, the “cyclic” application of strong gel treatments from time to time is understandable. This type of action has occurred before (Hild and Wackowski, 1999). Strong gels can wash out of fractured systems eventually, requiring retreatment.

5. Simulation

A number of simulation papers have claimed that CDGs (and other “flowing” crosslinked gels) have substantial potential to improve oil recovery (Gao et al., 1993; Gao and Burchfield, 1995; Smith et al., 2000; Xie et al., 2009; Castro et al., 2013; Manrique et al., 2014; Jahanbani Ghahfarokhi et al., 2016; Temizel et al., 2016; Temizel et al., 2018; Khamees and Flori, 2019; Izadi et al., 2020). These studies invariably assume (1) that the CDG (or other gel) flows deep into the reservoir and provides viscosity (resistance factor) like a polymer solution and/or (2) that the CDG/gel provides a significant permeability reduction (residual resistance factor) primarily (or exclusively) in the high-permeability zones. As pointed out earlier in this paper, neither of these assumptions are valid.

6. In-depth profile modification

An in-depth profile medication process has been developed and applied that relies on injection of a small water-like-viscosity bank of material that is strategically pushed into place with a water post-flush before activation (Fletcher et al., 1992; Sorbie and Seright, 1992; Seright et al., 2012). After placement, the material is activated (either thermally or by chemical reaction) to reduced flow capacity in the bank. Fig. 1 illustrates this process. In several versions of this process the injected material consists of suspensions of very fine (micron- or nano-sized) particles. In contrast to the CDG process, the in-depth profile modification process illustrated in Fig. 1 is a legitimate, viable process, although it is quite involved to implement (Seright et al., 2012). The “Bright Water” process (Pritchett et al., 2003) is the most well-known of this process. However, a number of other similar processes have been advocated (Temizel et al., 2017a,b; Dupuis et al., 2016; Yao et al., 2016; Zaitoun and Dupuis, 2017; Liu et al., 2019).

7. Overall summary

From this review, it is clear that there is no credible evidence that colloidal dispersion gels can propagate deep into the porous rock of a reservoir, and at the same time, provide resistance factors or residual resistance factors that are greater than those for the same polymer formulation without the crosslinker. Consequently, for CDG field projects, (1) money spent on crosslinker in the CDG formulations was wasted, (2) the mobility reduction/mobility control was under-designed, and (3) reservoir performance could have been damaged by excessive loss of polymer, face-plugging by gels, and/or excessive fracture extension.

CDGs have been sold using a number of misleading and invalid arguments. Very commonly, Hall plots are claimed to demonstrate

that CDGs provide higher resistance factors and/or residual resistance factors than normal polymer solutions. However, because Hall plots only monitor injection pressures at the wellbore, they reflect the composite of face plugging/formation damage, in-situ mobility changes, and fracture extension. Hall plots cannot distinguish between these effects—so they cannot quantify in situ resistance factors or residual resistance factors.

Laboratory studies—where CDG gels were forced through short cores during 2–3 h—have incorrectly been cited as proof that CDGs will propagate deep (hundreds of feet) into the porous rock of a reservoir over the course of months. In contrast, most legitimate laboratory studies reveal that the gelation time for CDGs is a day or less and that CDGs will not propagate through porous rock after gelation. A few cases were noted where highly depleted AI and/or HPAM fluids passed through cores after one week of aging. Details about these particular formulations/experiments were sparse and questions remain about their reproducibility. No credible evidence indicates that the CDG can propagate deep into a reservoir (over the course of weeks or months) and still provide a greater effect than that from the polymer alone.

With one exception, aluminum from the CDG was never reported to be produced in a field application. In the exception, Chang reported producing 1–20% of the injected aluminum concentration. The available evidence suggests that some free (unreacted) HPAM and aluminum that was associated with the original CDG can propagate through porous media. However, there is no evidence that this HPAM or aluminum provides mobility reduction greater than that for the polymer formulation without crosslinker.

Normal polymer flooding and gel treatments to reduce channeling through fractures still require improvements to provide the best effect, but at least they are technologies with a credible science and engineering basis. Because of the invalid claims and concepts associated with CDG technology, those applying CDG floods may reach overly negative conclusions if they equate results from CDG floods to those from legitimate polymer floods. The appeal behind the CDG claims is understandable. It would be a major advance if a “reversible crosslinking system” could be developed that would allow low concentrations of a crosslinker to substantially increase the effective viscosity of polymer solutions in porous media. However, a practical-such material remains to be developed.

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