# A Review of Polymer Gel Utilization in Carbon Dioxide Flow Control at the Core and Field Scale

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## Summary

Polymer gel has been used for water conformance control for several decades and may have significant potential in remediating unfavorable carbon dioxide ( $CO_2$ ) flow in the subsurface. High-mobility  $CO_2$  may channel quickly through sedimentary reservoirs, where unfavorable displacements are worsened in the presence of heterogeneities. Flow diversion technology targeting and withstanding  $CO_2$ is therefore essential to improving sweep efficiency and increasing storage potential. Polymer gel treatments have been demonstrated to remediate  $CO_2$  channeling in several enhanced oil recovery (EOR) field applications and have been proposed as a means to remediate wellbore and seal leakage during carbon sequestration. The goal of this review is to assess  $CO_2$  conformance control by polymer gel in published laboratory work related to both storage and EOR operations. Although field implementation of polymer gel has been successful in reducing  $CO_2$  flow, supporting experimental work on the laboratory scale is scattered, with both results and parameters varied. This paper summarizes the available literature and proposes a framework for future experimental work to aid more systematic assessment.

## Introduction

Injection of  $CO_2$  into sedimentary reservoirs for permanent storage purposes is, due to climate concerns and new incentives, increasingly important as an integral part of carbon capture and storage (CCS) value chains. Usage of anthropogenic  $CO_2$  for EOR, with simultaneous  $CO_2$  sequestration, may contribute to a timely upscaling of CCS and is here referred to as CCUS: carbon capture usage and storage.  $CO_2$ has already been used in EOR for several decades (Green and Willhite 2018), and despite inherent benefits, such as  $CO_2$ -oil miscibility achieved at low pressures, high  $CO_2$  mobility compared with reservoir fluids often leads to a rapid breakthrough, high cyclicity, and a poor sweep efficiency: recovering less oil than expected and storing less  $CO_2$  (Merchant 2017). The challenge of poor sweep efficiency is widely recognized and addressed in  $CO_2$  EOR, for example, by Al-Ali et al. (2013) stating that: "Sweep efficiency during  $CO_2$  flooding is typically the stumbling block to better application of  $CO_2$ -EOR technology." How the challenge is approached varies from drilling new wells to  $CO_2$  mobility and conformance control. A usual first approach to in-depth  $CO_2$  mobility control is the implementation of water alternating gas (WAG), where  $CO_2$  injection is spaced out by intermittent water injections to improve sweep efficiency. The entering of water into gasflooded zones and locally increased water saturation decrease gas relative permeability, in turn making it more likely that the next slug of injected gas will be diverted temporarily. In homogeneous reservoirs, this strategy may work well, but the efficiency of WAG is severely reduced in the presence of heterogeneities. Improved mobility control during  $CO_2$  floods in less uniform reservoirs may be achieved using  $CO_2$  foams (Alcorn et al. 2019), also with a varying degree of success (Borling 1994). In the presence of large-scale heterogeneities, such as fractures, polymer gels may be the most efficient means for  $CO_2$  diversion (W

Polymer gel is frequently used for water conformance control (Seright and Brattekas 2021) and has been implemented to control  $CO_2$  conformance on the field scale since the 1970s (Enick and Olsen 2012). The goal of the polymer gel treatment may be to reduce the permeability of highly permeable pathways while minimizing damage in the less permeable oil-bearing strata of the reservoir (Al-Ali et al. 2013), block large aperture fractures, and divert  $CO_2$  into adjacent matrix (Wassmuth et al. 2005) or remediate nonconformal flow behavior of  $CO_2$  within storage reservoirs (Durucan et al. 2016; Mosleh et al. 2016). Polymer gel technology has also been suggested as an option to treat leakage to shallow formations above a storage reservoir (Mosleh et al. 2017) and to remediate leakages in the caprock, where the generation of new fractures and reactivation of existing fractures and faults are concerns during  $CO_2$  injection due to increased pore pressure (Tongwa et al. 2013). A growing number of ongoing  $CO_2$  storage projects have not experienced leakage, and more than 99% of injected  $CO_2$  is expected to remain in the storage reservoir after 100 years (Daniels et al. 2023); however, methods for leakage remediation should be assessed and readily available.

Some recent works have advocated for polymer gel utilization in CCS and  $CO_2$  EOR: Massarweh and Abushaikha (2022) reviewed developments in  $CO_2$ -EOR mobility control, including WAG,  $CO_2$  foam, and nanoparticles, and briefly discussed and compared polymer gel systems for  $CO_2$  conformance [in-situ polymer gels and preformed particle gels (PPGs)]. Sun et al. (2020a) reviewed polymer gel, foamed gel, and PPG use in  $CO_2$  EOR. Different gel systems were described in detail, focusing on gel stability in acidic  $CO_2$  environments. Wellbore leakage and potential remediation by different gel systems was reviewed by Liu and Liu (2022) and Zhu et al. (2021). The two papers targeted CCS, but are also relevant for  $CO_2$  EOR. Zhu et al. (2021) focused on  $CO_2$  leakage remediation by a variety of sealant materials, such as cement, biofilms, gels, resins, foams, and nanoparticles. Liu and Liu (2022) identified polymer (including PPG), silicate, and  $CO_2$ -responsive gel systems as potential agents for gas leakage remediation and improved integrity in carbon injection wells. The reviews have so far mainly focused on gel mechanical strength and bulk properties, including gelation mechanisms,  $CO_2$  compatibility, and resistance to acidic conditions. While these factors are undoubtedly important, quantification of gel behavior during (injectivity/ propagation) and after (blocking ability) placement is equally important to improve  $CO_2$  conformance and leakage remediation.

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Laboratory experiments (most often on the core scale) are necessary to provide insight into the flow and blocking properties of different gels at realistic  $CO_2$  injection conditions. Several previous publications present experimental results to prove the abilities and efficiencies of a given gel system, often focusing on a limited number of influential parameters. The goal of this review is to summarize and systematically evaluate experimental assessments of  $CO_2$  flow diversion by polymer gel. Although polymer gel treatments show great potential in remediating  $CO_2$  flow, as demonstrated in several field applications, the supporting experimental work is scattered, with both results and parameters varied. Comparing polymer gel systems for use in CC(U)S therefore becomes challenging for researchers and operators alike. We will not distinguish between  $CO_2$  injections for geological storage and EOR, although the injected  $CO_2$  might come from different sources and polymer gel would be used for different reasons (leakage remediation in CCS vs. conformance control in CCUS). Both CCS and  $CO_2$  EOR require polymer gel systems able to divert or block  $CO_2$  over time, and the  $CO_2$  will be in supercritical phase for most reservoir conditions. This paper is divided into two sections, each targeting a specific issue where polymer gel has been proposed as a treatment option—*matrix* flow remediation (targeting channeling issues within a reservoir or overlying aquifer) and *fracture* flow remediation (targeting interwell communication and *seal* leakage through caprock fractures or faults).

CO<sub>2</sub> Conformance Treatment Using Polymer Gels—What Do We Want to Treat? Eight field implementations of polymer gel in CO<sub>2</sub> flow conformance are found in the literature (Table 1), and all relate to CO<sub>2</sub> EOR. Previous publications have focused on the technical aspects of injection and the outcome in terms of revenue (what volume and concentration injected over what duration and what was the payback in terms of economic lifetime of wells and well patterns). This insight is given elsewhere, e.g., Enick and Olsen (2012) provided a detailed summary of polymer gel treatments up to 2012, and Sun et al. (2020b) included more recent results. Publicly available data are probably not exhaustive, and polymer gel treatments may have been performed that are not published and therefore not covered by any of the reviews. [Enick and Olsen (2012) pointed to multiple nontechnical factors responsible for lacking implementation, upscaling, and publishing of CO2 conformance control by polymer gel.] CO2 flow diversion differs from water/oil application: (1) In-depth diversion of fluids into bypassed regions is required due to the high CO<sub>2</sub> mobility (Hild and Wackowski 1999). Shifting the conformance control strategy from near the wellbore to the reservoir has provided significantly improved results, and several "failures" in field implementation of conformance control may have been due to the application of a near-well, low-volume conformance strategy (Hild and Wackowski 1999; Enick and Olsen 2012; Borling 1994). [Hild and Wackowski (1999) pointed out that "while a [polymer gel] treatment that results in no apparent impact to injection or production is considered a failure, there have not been any other detrimental results, such as the loss of oil production, an increase in water or CO<sub>2</sub> production or a loss of effective injection support."] (2) The combination of CO<sub>2</sub> and brine forms a weak acid environment. Hence, dynamic flooding conditions may cause dissolution and erosion of carbonate rocks, and conformance challenges may not remain static but worsen during long-term CO2 injection; for example, the carbonate Anton Irish field (Larkin and Creel 2008; Smith et al. 2006), where initial fractures became substantial openings over time, extensive void space conduits several inches in diameter formed between injectors and producers, and prior near-wellbore treatments were much too small in volume to divert fluids from the massive void spaces. The acidic environment also has implications for the stability of polymer gel systems over time. In most field applications, WAG or foams were first implemented to control unfavorable CO<sub>2</sub> displacements, and polymer gel was used when the initial treatment did not have the desired effect, often due to the existence of significant heterogeneities, such as fractures or large vugs. The history of field applications (Table 1) clearly shows that polymer gel conformance control was never attempted to control the channeling of CO<sub>2</sub> in relatively homogeneous formations, yet core scale research has mostly been performed in unfractured, homogeneous core samples.

Field (Location)	Rock Type	What Was the Problem?	Polymer Gel Treatment	When?
Lick Creek field (Arkansas, USA)	Unconsolidated sand	Channeling through high- permeability thief zones	Hydrolyzed polyacrylamide (HPAM)/Cr(VI)	1978
		(Matrix permeability 1,200 md average, thief zones up to 3,000 darcies detected)	In-situ polymerized acrylamide monomer	1984
Rangerly Weber sand unit (Colorado, USA)	Sandstone	Fractures (not readily apparent during waterflooding)	High-molecular-weight HPAM/ Cr(III)-acetate	1994–1997
Wertz field (Wyoming, USA)	Sandstone	Natural fractures, oil-wet matrix	High-molecular-weight HPAM/ Cr(III)-acetate	
Anton Irish field (Texas, USA)	Carbonate	Long, large voids causing rapid interwell communication	HPAM solution	1991
		Fractures and dissolution due to $CO_2$ acidification	In-situ polymerized acrylamide monomer	1993
			High-molecular-weight HPAM- Cr(III)-propionate + foamed cement	2003
			Improved formulation	2005
			PPGs	2007
SACROC (Permian Basin, USA)	Limestone	Interwell communication; highly heterogeneous formation (lateral/vertical permeability discontinuities, microfractures, vugs)	PPG (superabsorbent crystallized copolymer); high-molecular-weight HPAM/Cr(III)-acetate	2007; 2010–2014

Table 1—Overview of the implementation of different polymer gel systems for CO<sub>2</sub> conformance at the field scale. Further technical details (references and outcome) may be found in Table A-1 of the appendix.

Field (Location)	Rock Type	What Was the Problem?	Polymer Gel Treatment	When?
Bat Raman field Limestone (Turkey)		Heterogeneous formation (fractures, vugs, and connecting cracks), viscous oil	Low-molecular-weight HPAM/ Cr(III)-acetate; high molecular- weight HPAM/Cr(III)-acetate	2002–2004
Permian's Slaughter field (Texas, USA)	Dolomite	Layered with significant permeability variations	In-situ polymerized acrylamide polymer	2000–2005
Brookhaven field	Unconsolidated sand (salt-cored)	Heterogeneities (182–5,830 md)	High-molecular-weight HPAM with unspecified organic crosslinker; HPAM concentration of 0.3–3–0.9 wt%	2008 2009

Table 1 (continued)—Overview of the implementation of different polymer gel systems for CO<sub>2</sub> conformance at the field scale. Further technical details (references and outcome) may be found in Table A-1 of the appendix.

*Matrix Flow Remediation.* Because polymer gels are permeability-reducing agents (Sydansk and Southwell 2000), we need to know *how much* the permeability to different injected fluids in porous rock is reduced (i.e., whether polymer gel reduces the flow of  $CO_2$  more or less than that of water and/or oil). Several laboratory studies have focused on polymer gel placement and resistance to subsequently injected  $CO_2$  in homogeneous outcrop or reservoir cores to assess permeability reduction.

Recent research (numerical and experimental) has also proposed matrix polymer gel treatments as an option for  $CO_2$  leakage remediation (to our knowledge not yet applied in fields), indirectly treating fractures and faults that extend into an overlying aquifer by treating the aquifer matrix with polymer gel. Hence, gel that forms above a leaking caprock may act like a new reservoir seal (Durucan et al. 2016; Mosleh et al. 2016, 2017). Numerical simulations of polymer gel injection into targeted zones above the caprock layer predicted successful fault sealing by polymer gel, stopping further  $CO_2$  leakage into the shallow aquifer. Simulations also indicated that polymer gel injection (with delaying agents) from a horizontal well close to a leaky fault and near the caprock could seal the caprock and remediate  $CO_2$ leakage (Mosleh et al. 2017). The idea of remediating leakage in a storage site by treating the overlying porous formation with polymer gel is interesting and may be possible with controlled and strategic placement from horizontal wells. Recent work should, however, be taken into account when assessing the practicality of this strategy, showing that mechanical degradation of polymers during placement may be less extensive than widely assumed, and hence injection pressures can quickly exceed the formation fracturing pressure (Sagyndikov et al. 2022; Seright et al. 2009). Injection of gelant above the fracturing pressure would infer a risk of fracturing the new seal and further diminish  $CO_2$  storage security. Gelant injection at lower pressures would keep the aquifer intact but could cause gel formation outside of the fault or fracture zone in which it is intended to be placed. Both the numerical assessment and planning of a storage site polymer gel treatment need to fully account for these potential pitfalls.

Fracture Flow Remediation. Fluid channeling through interconnecting fractures and fracture networks is a well-known conformance problem, even during injection of water (Seright and Brattekas 2021), and the problem intensifies during injection of highly mobile CO<sub>2</sub>. In some reservoirs, the presence of fractures is not apparent during waterflooding, but becomes clear during CO<sub>2</sub> injection (e.g., in the case of the Rangely Weber sand unit; Hild and Wackowski 1999). Field application overview (Table 1) clearly shows that reservoirs characterized by fractures, layering, and large-scale heterogeneities dominate the portfolio of polymer gel treatments for CO<sub>2</sub> flow control. Fracture channeling of CO<sub>2</sub> provides poor recovery efficiency, e.g., in the Weyburn field, where Wassmuth et al. (2005) stated that "gels should be considered as the conformance control technology with the most likely chance of success." Polymer gel injection was also proposed as a first step in integrated EOR for fractured reservoirs, where the fractures are blocked before subsequent injection of chase fluids, e.g., weak foam (Enick and Olsen 2012; Brattekås et al. 2013). In higher-permeability rock, the efficiency of a polymer gel fracture treatment is probably not uniquely different in CO<sub>2</sub> injections compared with waterfloods; success relies on the fracture being completely filled with gel (Brattekås et al. 2014), and the pressure the gel is able to withstand (rupture pressure), which depends on the polymer concentration. A higher concentration means higher polymer gel strength (Syed et al. 2014; Bai et al. 2007). Readers should note that polymer gel concentration can depend on the gel state during placement (Brattekås et al. 2015). Polymer gel is most often injected in the gelant state; a gelant is a mixture consisting mainly of water, with polymer and crosslinker added, that has properties similar to a polymer solution. When the gelant is subjected to an elevated temperature over time, it transforms into an elastic semisolid gel. Hence, depending on temperature and pumping time, gel may form during injection. Gelation time is defined as the main controlling parameter of gel penetration depth (Liu and Liu 2022) in matrix treatments. In fracture treatments, however, polymer gel will continue to propagate through fractures after formation. Hence, gelation time controls polymer gel propagation properties but does not necessarily limit the penetration depth. While gelant will likely channel through a conductive fracture, similar to a polymer solution, formed gel will propagate slower (via extrusion) due to water leakoff (Seright 2003; Brattekås et al. 2020). Water leakoff occurs due to the pressure differential between the gel in the fracture and the adjacent matrix and causes water to leave the polymer gel network and progress into the matrix, in turn, rendering the fracturefilling polymer gel more concentrated and pressure resistant. Note that polymer gel is often divided into two main categories in similar papers-in-situ polymer gels and PPG. Listed drawbacks of in-situ polymer gel often refer to the injected gelant state and do not consider the continued propagation of gel through fractures after formation. Water leakoff in fracture applications will cause an uneven polymer gel concentration in the fracture, where injected gel extrudes through concentrated gel within wormholes. Tongwa et al. (2013) noted that wormholes made gel less resistant to subsequently injected CO<sub>2</sub>. Previous findings using water as the subsequently injected fluid also show that wormholes are the most likely points of rupture within a gel-filled fracture (Brattekås et al. 2017); however, the concentrated gel around the wormholes maintained a high blocking ability also after rupture (Brattekås et al. 2015).

Storage sites additionally target  $CO_2$  leakag, a potential problem in CCS for which mitigation and remediation techniques are needed (Tongwa et al. 2013). Increased pore pressures during  $CO_2$  injections may lead to opening or reopening of fractures and faults in the caprock, through which  $CO_2$  can leak. Treating fractures through very low permeability rock with polymer gel is possible, but the propagation, placement, and pressure resistance of polymer gel in such systems will be different and more challenging compared with fracture treatments through higher-permeability rock, hence calling for new experiments.

#### **Summary of Core Scale Research**

**Table 2** shows an overview of laboratory scale experiments targeting  $CO_2$  conformance control. Experimental work is listed by category: whole cores and unconsolidated systems, fractured cores, and low-permeability samples (relevant to seals) with fractures. There are a



Fig. 1—Experimental conditions investigated. Black dots indicate that whole cores have been used in the study. Open dots indicate fractured core experiments. The majority of fracture experiments have been performed with  $CO_2$  in the supercritical phase.  $CO_2$  will be in the supercritical phase at most reservoir conditions.

significant number of variables in the performed experiments, both related to the core material (permeability, wettability, and saturation), but also including temperature and pressure conditions, injection rates/volumes, polymer and crosslinker type and concentration, shut-in times, presence of oil, and injected chase fluid (water or  $CO_2$ : phase, volume, rate, and duration). Experimental temperature and pressure conditions (**Fig. 1**) determine the  $CO_2$  phase (gas, liquid, and supercritical), which has implications for system acidity and polymer gel stability. The significant variations may be a consequence of experimental studies being performed in conjunction with field applications, where temperature and pressure conditions are set to match the reservoir conditions. The majority of fracture experiments have been performed with  $CO_2$  in the supercritical phase, while matrix experiments have used both gaseous and supercritical  $CO_2$ .

	C	erties		Experimental					
		Permeability (md)			Cor	nditions	Polymer Gel System		
System	Core Material	K <sub>abs</sub>	$K_{CO2}$ (* $K_{frac}$ )	Porosity (%)	<i>T</i> (°C)	P (kPa)	Polymer/ Crosslinker	Conc. (Polymer, Crosslinker)	Chase Fluid
Martin and Kova	rik (1987)								
Whole outcrop cores	Berea sandstone	141	13.8		40.6	10 342	High-molecular-weight HPAM-Cr(III)-acetate		
							Xanthan/Cr(III)		
							In-situ polymerized acrylamide monomer		
Martin et al. (198	38)								
Whole outcrop cores	Berea sandstone	348	55	19.3	40.6	10 342	Resorcinol-formaldehyde	Brine, WAG	
							Borate crosslinked polyvinyl alcohol		
							Borate crosslinked polyvinyl alcohol		
Seright (1995)									
Whole outcrop cores	Berea sandstone				41	6205–10 342	"Weak" phenoplast from resorcinol-formaldehyde		Brine, WAG

Table 2—Overview of experimental work performed to assess polymer gel efficiency in  $CO_2$  conformance. Several variables are present in experiments. Chase fluids vary from alternate brine,  $CO_2$ , and foam ( $CO_2$ -EOR applications) to single-phase  $CO_2$  ( $CO_2$  leakage remediation). Polymer and crosslinker concentration units are consistent with the cited publication [given in parts per million (ppm), percentage (% or wt%), or weight (mg/L)].

	Core Properties		Experimental						
		bility (md)	)	Conditions		Polymer Gel System			
System	Core Material	Kaba	$K_{CO2}$ (* $K_{troo}$ )	Porosity (%)	T (°C)	P (kPa)	Polymer/ Crosslinker	Conc. (Polymer/ Crosslinker)	Chase Fluid
					. ,		"Strong" phenoplast from resorcinol-formaldehyde	,	
							Xanthan/Cr(III)		
							High-molecular-weight HPAM-Cr(III)-acetate		
Raje et al. (1996)									
Whole outctrop cores	Berea sandstone				32–41	8274	Alcaligenes polysaccharide		
Syed et al. (2014	)								
Whole outcrop cores	Doddington sandstone		2,171		40	350	Low-molecular-weight HPAM-Cr(III)-acetate	6%/ 50,000ppm	CO <sub>2</sub>
			1,928		40	350	Low-molecular-weight HPAM-Cr(III)-acetate	4.1%/ 50,000ppm	
			2,147		40	350	Low-molecular-weight HPAM-Cr(III)-acetate		
			1,936		40	350	Low-molecular-weight HPAM-Cr(III)-acetate		
Durucan et al. (20	016)						-		
Whole outcrop cores	Guilting carbonate		670	30	40	380	High-molecular-weight HPAM/Zr+	1,000/ 15 ppm	CO <sub>2</sub>
	Doddington sandstone		579	15					
Mosleh et al. (20	16)								
Whole outcrop cores	Doddington sandstone		352	15	22	Ambient	High-molecular-weight HPAM/Zr+	1,000/ 50 ppm	CO <sub>2</sub>
			450	15	40	Ambient	High-molecular-weight HPAM/Zr+	600/15 ppm	
			619	16	60	Ambient	High-molecular-weight HPAM/Zr+	600/15 ppm	
			2,180	20	40	Ambient	Low-molecular-weight HPAM-Cr(III)-propionate	21,000/ 50,000 ppm	
			1,928	20	40	Ambient	Low-molecular-weight HPAM-Cr(III)-propionate	41,000/ 50,000 ppm	
Sun et al. (2021)									
Whole outcrop cores	Berea sandstone	107		18.2	45	Above supercritical	High-molecular-weight HPAM-Cr(III)-acetate	5,000/ 417 ppm	CO <sub>2</sub> , WAG
		282		22.5				7,500/ 417 ppm	
		350		23.1				10,000/ 417	
		431		21.5				ppin	
		1 225		27.5					
		402		22.2					
		425		23.1					
		120		20.1					
Whole outcrop	Sandstone	20.6		17.3					
cores	Sandstone	2.350		18 9	30	3000	NC/ethylenediamine (CO <sub>2</sub> -		CO
Martin and Kovar	ik (1987)	2,000		10.3					002
Whole receiver	in (1007)		10.7	10		6205			
cores			13.8	12		0200			Brine, WAG
Topgüder (1999)			10.0						

Table 2 (continued)—Overview of experimental work performed to assess polymer gel efficiency in  $CO_2$  conformance. Several variables are present in experiments. Chase fluids vary from alternate brine,  $CO_2$ , and foam ( $CO_2$ -EOR applications) to single-phase  $CO_2$  ( $CO_2$  leakage remediation). Polymer and crosslinker concentration units are consistent with the cited publication [given in parts per million (ppm), percentage (% or wt%), or weight (mg/L)].

	C	erties		- Expe	rimental				
		Permea	ability (md)	_	Con	ditions	Polymer Gel S	ystem	
System	Core Material	K <sub>abs</sub>	$K_{\rm CO2}$ (* $K_{\rm frac}$ )	Porosity (%)	<i>T</i> (°C)	P (kPa)	Polymer/ Crosslinker	Conc. (Polymer/ Crosslinker)	Chase Fluid
Whole reservoir cores					60		High-molecular-weight HPAM-Cr(III)-acetate		
							High-molecular-weight HPAM-Cr(III)-acetate		
							Low-molecular-weight HPAM-Cr(III)-acetate		
Wassmuth et al.	(2005)								
Unconsolidated	Crushed carbonate				<60	6900	High-molecular-weight HPAM-Cr(III)-acetate		
Taabbodi and As	ghari (2006)								
Unconsolidated	Crushed carbonate		12,238	34.5	40	8274	High-molecular-weight HPAM-Cr(III)-acetate	7,500/ 300 ppm	CO <sub>2</sub> , WAG
			2,398	33.7			High-molecular-weight HPAM-Cr(III)-lactate	7,500/ 300 ppm	Brine, WAG
			10.000	05.0			Low-molecular-weight	5 wt%/	Brine,
			0 410	30.Z			HFAM-CI(III)-acelale	0.417 W1%	WAG
Luc et el (2022)			2,410	35.5					
		400							
Artificially layered	Sandstone	800, 2,400		32.9	45	10 000	UC22AMPM (CO <sub>2</sub> responsive surfactant)	2.1 wt%	CO <sub>2</sub> , WAG
Wang et al. (201	9)								
Fractured (longitudinal, 0.5 mm open)	Berea sandstone	50 (±4.5)		18.5	60	7584	CR-PPG (CO <sub>2</sub> responsive gels)		
Sun et al. (2020a	a)								
Partially fractured	Berea sandstone				45	7584	PPG		
Wassmuth et al.	(2005)								
Fractured (longitudinal, filled with	Indiana		*1 200				High molecular weight		
beads)	limestone	100	2,100		<60	17 000	HPAM-Cr(III)-acetate		
Al-Ali et al. (2013	3)								
Fractured	Limestone	70	*2,100		48.9	11 721	HIGH-MOIECUIAr-Weight HPAM-Cr(III)-acetate	3,000/ 300 ppm	
Brattekas et al. (2	2013)								
Fractured (longitudinal 1 mm open)	Oil-wet Edwards limestone				ambient	ambient	High-molecular-weight HPAM-Cr(III)-acetate	5,000/ 417 ppm	CO <sub>2</sub> foam
Xiao et al. (2016)	)								
Fractured (longitudinal)	Reservoir	50		17	60	12 410	High-molecular-weight HPAM-Cr(III)-acetate	900–1000/ 60–80 mg/L	
Tongwa et al. (20	013)								
Fractured (longitudinal	Lamotte sandstone		1.82	16		10 342	High-molecular-weight HPAM-Cr(III)-acetate		CO <sub>2</sub>
u.5 mm open)	Bonneterre dolomite		0.002	3		10 342			
	Davis shale		0.0004	10		10 342			
	Derby-Doerun shaly dolomite		4.00×10 <sup>-5</sup>	1		10 342			
Syed et al. (2014	-)								

Table 2 (continued)—Overview of experimental work performed to assess polymer gel efficiency in  $CO_2$  conformance. Several variables are present in experiments. Chase fluids vary from alternate brine,  $CO_2$ , and foam ( $CO_2$ -EOR applications) to single-phase  $CO_2$  ( $CO_2$  leakage remediation). Polymer and crosslinker concentration units are consistent with the cited publication [given in parts per million (ppm), percentage (% or wt%), or weight (mg/L)].

	Core Properties				Experimental				
		Permea	bility (md)		Cor	nditions	Polymer Gel System		
System	Core Material	K <sub>abs</sub>	$K_{\rm CO2}$ (* $K_{\rm frac}$ )	Porosity (%)	<i>T</i> (°C)	P (kPa)	Polymer/ Crosslinker	Conc. (Polymer/ Crosslinker)	Chase Fluid
Fractured (longitudinal,	Marble core (nonpermeable)		*8,100		40		Low-molecular-weight HPAM-Cr(III)-acetate	2.1%/ 50,000 ppm	
closed)			*8,100		40		Low-molecular-weight HPAM-Cr(III)-acetate	4.1%/ 50,000 ppm	
			*8,100		40		Low-molecular-weight HPAM-Cr(III)-acetate	6.0%/ 50,000 ppm	
Pu et al. (2021)									
Fractured		0.96		9.9					
(longitudinal, 0.2 mm)	Baikouquan	0.85		9.9			IPN-PAASP (CO -		
	reservoir cores	0.89		10.1	68	Ambient	responsive PPG)	5000 mg/L	CO <sub>2</sub>

Table 2 (continued)—Overview of experimental work performed to assess polymer gel efficiency in  $CO_2$  conformance. Several variables are present in experiments. Chase fluids vary from alternate brine,  $CO_2$ , and foam ( $CO_2$ -EOR applications) to single-phase  $CO_2$  ( $CO_2$  leakage remediation). Polymer and crosslinker concentration units are consistent with the cited publication [given in parts per million (ppm), percentage (% or wt%), or weight (mg/L)].

Previous literature (Tables 1 and 2, including most field treatments) has used variations of (poly)acrylamide polymer/inorganic crosslinker gel systems, due to accessibility and applicability in a wide variation of conformance problems (ability to form flowing to rigid gels depending on its concentration. Note that organic crosslinkers may also yield rigid and flowing gels and have more flexibility in terms of temperature and salinity). The most common CC/AP (acrylamide polymer crosslinked by chromium acetate or propionate) gel system is applicable over a broad pH range (pH > 2-12) when properly formulated and, hence, applicable in conjunction with acidic CO<sub>2</sub> flooding (Sydansk and Southwell 2000). The CC/AP gel system was chosen for application in the Wertz field partly due to its long-term gel stability in H<sub>2</sub>S and CO<sub>2</sub> environments (Borling 1994) and deemed appropriate for the Rangely field because of its insensitivity to the low pH characteristic of CO<sub>2</sub> floods if the degree of hydrolysis of the polymer is in the appropriate range (Enick and Olsen 2012). Wassmuth et al. (2005) advocated for CC/AP gel formulations as a "robust alternative" to block fractures and divert the subsequently injected CO<sub>2</sub> into the matrix. Laboratory studies in recent years, however, do not fully agree on the applicability of the CC/AP system in CO2 conformance: Sun et al. (2021) expressed surprise over the success of field performance of Cr(III)/HPAM gels based on laboratory findings where the gel system did not hold well when exposed to CO2 (Sun and Bai 2017; Sun et al. 2018). Readers should note that gel systems are under development that might be more resistant to CO<sub>2</sub> acidic conditions over time (Sun et al. 2020a) and/or require acidic conditions to form. Wang et al. (2019) investigated the performance of CO<sub>2</sub>-responsive PPG (the gels swell in contact with CO<sub>2</sub>) in fractures of 0.5-mm aperture and found it to be stable for 6 months in the presence of water and CO<sub>2</sub>. In comparison, CC/AP gels have also performed well in similar tests, e.g., Tovar et al. (2014) measured the degradation of polymer gel [copolymers of acrylamide/acrylate and acrylamide/2acrylamido-terbutylsulfonic acid (ATBS)] during aging in contact with CO<sub>2</sub> and compared results with gel samples exposed to N<sub>2</sub> gas. They found that conventional polymers were applicable in CO2 EOR in low divalent cation water and a reservoir temperature of up to 50°C. Tongwa et al. (2013) tested the chemical stability of polymer gel: The gel was exposed to CO<sub>2</sub> and sealed for 7 months. No changes were observed in gel flow behavior for any concentration, and the gel mechanical strengths were the same as at the beginning of the measurements. The authors therefore concluded that CC/AP gels were stable in CO<sub>2</sub> environments for this time period. Al-Ali et al. (2013) and Durucan et al. (2016) used CC/AP gels in core scale experiments and found it more resistant to acidic conditions than other gels, which were limited to certain pH conditions (borate crosslinked guar; Al-Ali et al. 2013) or chemically degrade at higher temperatures (biopolymers; Durucan et al. 2016). Syed et al. (2014) concluded that CC/AP gel systems can be used in CO<sub>2</sub> applications based on corescale experiments. Gel stability in CO<sub>2</sub> environments was explained in detail by Sun et al. (2020b) and will not be revisited herealthough varying experimental conditions may be partly responsible for disagreements regarding gel chemical stability (experimental conditions influence CO<sub>2</sub> phase and acidity). While acknowledging the importance of gel stability in field treatments (especially in CCS leakage remediation), we will focus on polymer gel performance in coreflooding experiments. The experimental work was usually conducted over shorter periods of time, where chemical stability was not a major influence.

**Remediating Matrix Flow.** Fourteen experimental publications targeted matrix flow remediation by polymer gel (**Table 2**). Twelve of the studies used sedimentary rock cores, while two used unconsolidated crushed carbonate packs. Although the purpose of polymer gel treatments is different in pure CO<sub>2</sub> storage projects compared with CO<sub>2</sub>-EOR projects, the core-scale studies are similar, with some practical variables. CO<sub>2</sub>-EOR matrix polymer gel treatments have mainly aimed to improve WAG; hence, water and CO<sub>2</sub> have been alternately injected after the gel placement, often starting with the injection of water. In experiments targeting CO<sub>2</sub> leakage from a storage reservoir, pure CO<sub>2</sub> floods were performed after polymer gel placement.

The first published investigations of polymer gel remediation of  $CO_2$  flow date back to the late 1980s (Martin and Kovarik 1987; Martin et al. 1988) and became the template after which later matrix experiments were performed. The experimental schedule is relatively simple: First, cores were saturated and baseline saturations were established. This step includes one to three injected fluids, depending on the study; some cores were fully saturated by water, some were saturated by water and reservoir oil, and some injected  $CO_2$  to measure the effective gas permeability. Gelant was thereafter injected into the cores and a shut-in period followed to form gel. Chase fluids were finally injected, also varying between one to three fluids (water, oil, and  $CO_2$ ). Pressures were monitored during all steps in the initial studies, to assess gel rupture and blocking ability after rupture compared with pre-gel treatment values, enabling calculation of the residual resistance factor (RRF: the ratio of the permeability before the gel treatment to the permeability after, while flowing the same fluid), which can be used as a measure of gel treatment efficiency. Many subsequent studies have kept a similar experimental schedule, and the experimental results can therefore be compared (**Figs. 2 and 3**). Measured RRF values in three matrix studies that used modifications of the same polymer gel system are shown in **Fig. 2**.



Fig. 2—WAG after CC/AP gel placement in sandstone. The x-axis starts at the first CO<sub>2</sub> injection. Multiple corefloods are presented in most papers (duplicate paper listings). The RRF values are provided in the appendix, Table A-2.



Fig. 3—RRF for matrix experiments using variations of the CC/AP gel system. The gray area represents RRFs for whole cores (also shown in Fig. 2). Data points represented are from papers that have reported RRF, or provided pressure measurements or percentile decrease in CO<sub>2</sub> flow through the core enabling RRF calculation. Studies focused on recovery (presenting effluent production without pressure data) were not suitable for comparison. Polymer gel consistently reduced CO<sub>2</sub> flow more than water flow in unconsolidated systems (red, circular markers). Absolute permeability (brine) or effective CO<sub>2</sub> permeability measurements were used to represent "K before" in RRF calculations, which seemed to make a considerable impact on the reported RRF values. We propose that both permeabilities are reported when measured and authors are clear on which value is further used in calculations.

In **Fig. 2**, note that the RRF was commonly greater for brine injection than for  $CO_2$  injection. In flow through matrix, this behavior is detrimental to a WAG process because  $CO_2$  ultimately has an accentuated mobility relative to that of water. For improved WAG, the polymer gel must reduce  $CO_2$  mobility notably more than brine mobility. Thus, none of the polymer gels in **Fig. 2** improved the WAG process. This "disproportionate permeability reduction" also reveals that the polymer gels are generally more effective in blocking or reducing water flow than gas flow. In examining a particular phase in **Fig. 2**, the RRF commonly decreased from one WAG cycle to the

next, indicating a deterioration in the performance of the polymer gel. A considerable spread in reported RRF values can be seen, even though the same polymer gel system is used. This relates to several factors: Values below 10 are ascribed to early development [formulation development from Cr(VI) to more reliable Cr(III) crosslinker, and stability in the presence of CO<sub>3</sub>], and significant progress was made between the two baseline publications of Martin and Kovarik (1987) and Martin et al. (1988), going from "80% brine and 83.3% CO<sub>2</sub> permeability reduction initially, which was completely lost during the third WAG cycle" to a fairly constant CO<sub>2</sub> permeability after polymer gel placement and a more controlled permeability reduction related to gelling agent concentration. Seright (1995) further developed the experimental system with internal pressure taps and was able to measure gel behavior without influence from the inlet (first 2 cm of the core was regarded as a filter). Seright focused on the improvement of WAG using different polymer gel systems, and both brine and CO<sub>2</sub> were used as chase fluids. The polymer gel was ruptured by an initial brine flood, and CO<sub>2</sub> and brine were thereafter alternately injected. A substantial reduction in RRF was noted already during the first WAG cycle. Sun et al. (2021) also found significant gel degradation and dehydration during CO2 flow, and that the effect of polymer gel was negligible after two WAG injection cycles. The objective of their study was also to improve WAG, but the order of injected chase fluids was reversed and CO2 was first injected to break the polymer gel. The experimental results of Sun et al. (2021) and Seright (1995) are similar, both reporting a more extensive fluid limitation in low-permeability cores compared with higher-permeability cores, and indicating that the CO<sub>2</sub> breakthrough pressure increases with polymer concentration. The pressure profile in some of the experiments (Sun et al. 2021) could indicate that CO<sub>2</sub> gradually breaks through the core (e.g., due to polymer gel dehydration) rather than mechanically rupturing the gel and swiftly channeling through to the production end.

Breaking the polymer gel with CO<sub>2</sub> rather than water may arguably be more relevant to a broader range of CO<sub>2</sub> applications, including CCS and CO<sub>2</sub> leakage remediation studies. Note that continued CO<sub>2</sub> injection, without alternating water slugs, over time may accelerate gel dehydration. Durucan et al. (2016) performed laboratory corefloods to investigate if polymer gel can be used to remediate nonconformal flow behavior of CO<sub>2</sub> within storage reservoirs. They used different polymer gel systems (synthetic and biopolymers) and performed single-phase CO<sub>2</sub> injection after gel placement, hence only measuring one RRF value for CO<sub>2</sub>. They reported CO<sub>2</sub> permeability reduction in carbonate (from 670 to 1 md) and sandstone (from 579 to below 1 md or "more than 99% reduced") due to polymer gel treatments but did not state at what time the data were collected in relation to CO<sub>2</sub> breakthrough. Mosleh et al. (2016) also performed core-scale studies aimed at leakage remediation in five cores and reported CO2 permeability before and after polymer gel treatment but only reported the permeability endpoints. Thus, it is unclear how many pore volumes of CO2 were injected and how the pressure developed during injection. The RRF values calculated from the reported endpoints ranged from 77 to >1 million, showing the greatest reduction of CO<sub>2</sub> flow in cores with the highest initial permeabilities, opposite to the findings of Seright (1995) and Sun et al. (2021). Note that Seright and Sun et al. used pressure conditions that corresponded to supercritical CO2, while Durucan and Mosleh used ambient conditions where CO2 is in the more compressible gas phase. The solubility of CO<sub>2</sub> in water increases with pressure and decreases with temperature for the experimental conditions in Fig. 1, which could influence polymer gel dehydration and stability. Syed et al. (2014) also used gaseous CO<sub>2</sub> to investigate the influence of salinity and HPAM polymer concentration on flow reduction and found that stronger gels (higher polymer concentration) reduced CO<sub>2</sub> permeability more, where the permeability reduction varied from 89.1% to 99.9%. Some authors therefore proposed to significantly increase the polymer concentration in the last injected slug, to increase the CO<sub>2</sub> breakthrough pressure. Topgüder (1999) aimed experimental work at the Bat Raman formation, a fractured limestone reservoir where polymer gel was used to provide conformance control in high-permeability zones. They used ambient pressure and whole reservoir cores in their study, and two approaches were used: (1) small volume, "strong" polymer gel treatment for the near wellbore and (2) large volume, "weak" polymer gel treatment for in-depth. The chase fluid was pure CO<sub>2</sub>. Pressure drops and effluent monitoring were used to assess CO<sub>2</sub> conformance success, compared with the baseline water injection pressure (30 psi). The differential pressure increased to 1,800 psi (weak polymer gel injection) and 1,980 psi (strong polymer gel injection) and also steadily increased during CO<sub>2</sub> injection. For weak polymer gel, CO<sub>2</sub> breakthrough occurred at 2,100 psi, but when the pressure was reduced to 1,850 psi, gas production ceased. For strong polymer gel, no gas production was observed at a differential pressure of 1,910 psi. Pressure gradients would provide a better foundation for comparison with other studies, but the paper did not provide enough information to convert the measurements to gradients.

Sun et al. (2021) provided an example of the use of laboratory measurements. They performed a numerical study where the hypothetical reservoir was layered without crossflow or fractures, and gelant was assumed to penetrate only into the high-permeability layer. In this case, methods like mechanical isolation of zones must be used to confine the flow reduction to the offending channel. Otherwise, as gelant flow in porous media is governed by Darcy's law, the gelant could enter and cause substantial damage to oil-bearing zones (Seright and Brattekas 2021). After assuming effective polymer gel placement, the simulations assume that  $CO_2$  cannot enter into the highpermeability zone as long as the fluid pressure remains below the gel breakthrough pressure. If the  $CO_2$  pressure increases above the gel breakthrough pressure,  $CO_2$  flow in the high-permeability layer depends on the gel RRF to  $CO_2$ . The significant spread in experimental values (**Fig. 2**) shows us that a generic value for  $CO_2$  RRF will be difficult to predict.

Wassmuth et al. (2005) and Taabbodi and Asghari (2006) also used matrix experiments to investigate the efficiency of polymer gel in  $CO_2$  conformance control but used unconsolidated, crushed carbonate porous media instead of consolidated cores. Wassmuth et al. (2005) saturated and flooded the porous media with water, oil, and  $CO_2$  before the implementation of conformance control and compared the breakthrough pressure of  $CO_2$  in a polymer gel-treated system to foam, polymer-enhanced foam, and foamed gel systems. They found that the polymer gel system consistently provided the most efficient conformance control to both gas and water, with a reported RRF near 5,000 for water. The paper is mainly focused on oil recovery (increased oil recovery during subsequent  $CO_2$  flooding was observed after placement of polymer gel) and does not provide enough data to extract RRF values. Taabbodi and Asghari (2006) used polymer gel to improve WAG and provided more measurements. Gelant was placed in a fully water-saturated system and shut in to form gel before cyclic injection of several pore volumes of water and  $CO_2$ . Polymer gel reduced both water and  $CO_2$  permeabilities, where the reported RRF values (Fig. 3) indicate that  $CO_2$  permeability was consistently reduced more than the permeability of injected water. This reported behavior contrasts dramatically with other reports, where water permeability was consistently reduced more than  $CO_2$  permeability (Seright 1995; Martin and Kovarik 1987; Martin et al. 1988; Sun et al. 2021; see Fig. 2). The authors allude to wettability as an explanation, defining water as the nonwetting phase, but wettability measurements or supporting evidence is not shown in the paper. We also note that the experiments in the work from Taabbodi and Asghari (2006) used more concentrated polymer gels than other work. Perhaps this factor also played a role in changing the RRF behavior. Clearly, this is an interesting phenomenon to pursue in future research.

Important questions that are investigated through matrix (whole core) laboratory experiments include the following:

• Does polymer gel reduce porous media permeability to CO<sub>2</sub>?

• Does polymer gel reduce the permeability of CO<sub>2</sub> more than the permeability of water?

All publications clearly show that polymer gel reduces porous medium permeability to  $CO_2$ , although the extent and duration of the permeability reduction vary. Several authors studied the effect of polymer gel on  $CO_2$  conformance, but the variation in results (RRFs)

due to the use of different gel, rock/fluid systems, and experimental conditions is significant. Most published works set out to find the CO<sub>2</sub>-blocking ability for a specific polymer gel system, or reservoir, and did not consistently report the data necessary to compare the results with other works or understand polymer gel mechanistic during CO<sub>2</sub> blocking attempts. When it comes to the second question: Does polymer gel reduce the permeability of CO<sub>2</sub> more than the permeability of water? it is widely known that polymer gel tends to reduce the permeability of water more than the permeability of oil. Whether this differentiation is also applicable to CO<sub>2</sub> is interesting for the design and implementation of polymer gel treatments in CO<sub>2</sub> EOR and CCS. While the higher reduction of permeability to water is advantageous in oil/water systems, a higher reduction in CO<sub>2</sub> flow compared with water would be favorable in polymer gel treatments aiming to reduce the flow and cycling of CO<sub>2</sub>. Seright (1995) and Sun et al. (2021) observed disproportionate reductions in permeability in their works, and polymer gels were found to reduce the permeability of water much more than that of CO<sub>2</sub>, as expected. Sun et al. (2021) found that the disproportionality was more pronounced in the cores in the lower-permeability range (range investigated was K =107-1,225 md). The disproportionate reduction in favor of CO<sub>2</sub> reported by Taabbodi and Asghari (2006) was consistent in three experiments, which suggests that the used system is also consistently different from previously investigated matrix systems. There are only two studies that reported using unconsolidated core material, and these are also the only two where CO2 and brine are alternately injected after polymer gel placement in a carbonate system. Hence, the deviation from the expected disproportionality (consistently reducing water more than gas), as shown in Fig. 3, may relate to the core material (rock type), the unconsolidated nature of the material (unknown stability, gel may encapsulate grains completely, hence changing the properties of the grain surfaces effectively altering the porous medium properties), or wettability (the used oil).

Other polymer gel systems have also been investigated using the same experimental framework. Raje et al. (1996) developed a biopolymer system (KUSP1) where the objective was to reduce the permeability in high-flow zones and divert CO2 to lower-permeability zones. Injection of supercritical CO2 into KUSP1 saturated cores caused in-situ gelation and reduced the permeability to CO2 with about 85% of the initial effective CO<sub>2</sub> permeability. Luo et al. (2023) developed a CO<sub>2</sub>-responsive surfactant system that would gel after being in contact with CO<sub>2</sub> for some time (hours). The system was tested during WAG injection in an artificial, layered core and compared with conventional WAG in a duplicate core. They found that the differential pressure increased during WAG injection after CO<sub>2</sub>-responsive surfactant placement, interpreted as blocking of high-permeability layers by polymer gel, and reported an endpoint plugging efficiency to brine of 96%. Pressure gradients were consistently lower during CO2 slugs compared with water slugs, indicating a disproportionate better blocking of water compared with CO2, although the global differential pressure measurements do not allow distinguishing of local displacements within the different layers. Raj et al. (2021) prepared a CO<sub>2</sub>-responsive nanocellulose gel for mobility control and tested its performance in high- and low-permeability sandstone with oil present. The pressure response across each core varied greatly; the authors concluded-perhaps prematurely-that the gel could work better for low-permeability systems, and that the low effect in the highpermeability core was due to incomplete blocking of larger pores. However, no evidence was produced to confirm this mechanism. Wang et al. (2019) and Sun et al. (2020a) developed CO2-responsive or -resistant PPGs for use in CO2 conformance control. PPGs are not suited for matrix treatments due to the short penetration depth of the gel particles in porous media, and the gel systems were therefore often tested in hybrid (partially fractured) systems. Interpretation of hybrid systems in the context of matrix and fracture remediation should be done with caution, as the results will be impacted by both matrix and fracture properties.

**Remediating Fracture Flow.** This section will be divided into two; fracture treatments in CCUS and CCS are significantly different because the permeability of the matrix adjacent to the fracture corresponds to a producing reservoir ( $CO_2 EOR$ ) or a seal (CCS). The permeability difference will influence polymer gel dehydration during fracture propagation. Note that gel stability requirements also differ: Seal leakage remediation requires successful blocking over a significant time scale (ideally: permanent); hence, stable materials are required. Again, several publications applied variations of the CC/AP gel system for CCUS and CCS fracture applications to improve subsequent  $CO_2$  floods in fractured carbonates (Wassmuth et al. 2005; Brattekås et al. 2013; Al-Ali et al. 2013) or reservoir cores (Xiao et al. 2016), or to remediate fractured seals (Tongwa et al. 2013; Syed et al. 2014).

**Remediating Fractured Seals.** Tongwa et al. (2013) and Syed et al. (2014) applied polymer gel to block fractures through very lowpermeability cores relevant to seals, to investigate the potential for sealing  $CO_2$  leakage pathways during  $CO_2$  sequestration in saline aquifers. Tongwa et al. (2013) compared polymer gel with other fracture-sealing materials, such as paraffin wax, silica-based gel, and microcement, by comparing the fracture pressure of a core where the fracture is sealed to the fracture pressure of an intact concrete core. The pressure necessary to reopen a sealed fracture will give an indication of the applicability of the material in the field during  $CO_2$ injection. The sealing materials were tested in fracture apertures ranging from 0.25 to 1 mm, and polymer gel was found to have a fairly low breakdown pressure of 265 psi in the 20-cm-long core (i.e., a pressure gradient of 9136 kPa/m). The polymer gel was found to reduce the flow of brine in narrow fractures (0.25-mm aperture) but could not completely block the fracture to achieve matrix permeability in 0.5- or 1-mm wide fractures. Note that the matrix permeability was very low (**Table 2**); hence, this restriction in fracture width does not apply to conformance control within a reservoir. The authors noted that polymer gel was a less effective sealant agent due to the formation of wormholes. Syed et al. (2014) used a fracture surfaces, after which the cores were assembled in a core holder; the actual fracture permeability in experiments may therefore have been difficult to control. The authors report RRF values for the fractured system ranging between RRF = 13 and 338.

**Remediating Fracture Flow in CO**<sub>2</sub> **EOR for CCUS.** As previously pointed out (Seright 1995), high RRFs correspond to very high pressure gradients in matrix applications (i.e., gelant that penetrates radially into the rock matrix around an unfractured well and forms gel with high RRF will stop flow). High RRF may have a more practical function in fractured wells, where the goal is to block the fracture and divert subsequently injected fluids into the matrix. Eight papers are published where the aim of the study was to block fractures, six applying CC/AP gel and two applying PPGs. This is a surprisingly limited number of publications, relative to how widespread fracture channeling is (Table 1). The experimental works reflect a significant span in both parameters investigated and methodologies used. Several papers use hybrid matrix/fracture core systems and imaging rather than pressure measurements to assess flow patterns, rendering direct comparison between studies difficult.

Sun et al. (2020a) and Wang et al. (2019) investigated the performance of CO<sub>2</sub>-responsive PPGs in fractures. The PPG swells in contact with CO<sub>2</sub>; hence, conformance control can improve during dynamic CO<sub>2</sub> injection. Sun et al. (2020b) used a hybrid system (partially fractured), and the measured differential pressure was therefore impacted by the properties of both the matrix (two-phase saturated) and fracture (PPG filled). RRF values reported (ranging from RRF = 1 to 400) are not directly comparable with other systems with longitudinally open fractures spanning the length of the core. Wang et al. (2019) found that the same PPG blocked longitudinal fractures and remained stable for 6 months in acidic water/CO<sub>2</sub> conditions. They reported very high CO<sub>2</sub> RRFs in the range of RRF =  $2-6 \times 10^7$  after CO<sub>2</sub> breakthrough, where the variation mainly seemed to depend on the shut-in time after PPG injection. CO<sub>2</sub>-responsive PPGs are only

suitable to treat fractures; the gel particles did not enter the porous matrix but resided on the injection end face of the core when the same PPG was used in matrix experiments. With PPG present on the end face, Wang et al. (2019) measured RRFs of 430 in matrix systems. When the external gel was removed, the RRF dropped to 58.5, and after the removal of the first millimeter of core material, a drop to 2.75 was measured, confirming the limitation of PPGs to fracture treatments. A similar observation was made by Pu et al. (2021), who observed that the injection pressure increased very fast when trying to force  $CO_2$ -responsive PPGs into the matrix. They further used longitudinally fractured cores, with granular fill, to measure  $CO_2$  plugging efficiency in a tight core.  $CO_2$ -responsive PPG and  $CO_2$  were alternately injected into the fracture, during which the injection pressure significantly increased. Single-phase  $CO_2$  was injected after PPG gel placement and aging; the blocking efficiency was reported to be 99%, and the pressure gradient after two fracture volumes of  $CO_2$  injected was 3750 kPa/m. When oil was included in the study, the stable pressure gradient during  $CO_2$  injection decreased to about 1600 kPa/m. Comprehensive investigations were not performed, and it remains unclear whether the blocking ability will improve or decrease due to  $CO_2$  breakthrough and continuous contact of polymer gel with  $CO_2$ .

The fracture-blocking efficiency of most CC/AP gel systems depends on the gel state during placement (Brattekås et al. 2015). Four publications applied variations of the CC/AP gel system to control CO2 fracture channeling in CO2 EOR to improve subsequent floods in fractured carbonates (Wassmuth et al. 2005; Brattekås et al. 2013; Al-Ali et al. 2013) or reservoir cores (Xiao et al. 2016). Wassmuth et al. (2005) investigated polymer gel efficiency in fractured limestone cores and compared the results with polymer-enhanced foams and foamed polymer gels. The gel was placed in the gelant state. The performance of CO<sub>2</sub> conformance control (polymer gels, polymer enhanced foams, and foamed polymer gels) was deduced from pressure measurements, where both the breakthrough pressure and pressure drop during extended CO<sub>2</sub> flooding were recorded. Wassmuth et al. (2005) targeted the Weyburn formation and rightfully stated that "since Weyburn is a fractured/heterogeneous reservoir, it was relevant to evaluate mobility control, blocking and diverting ability in cores with such extreme permeability contrasts." Straight polymer gel applications consistently provided the greatest resistance factors to the flow of both gas and water in fractured cores. In their experiments, the open fracture (aperture of 0.5 mm) was filled with glass beads, which creates a dual-porosity system where the fracture permeability was 13-21 times higher than the matrix permeability. Due to the high permeability contrast, more than 99% of the injected brine initially channeled through the open fracture. Wassmuth et al. (2005) suggested that any oil recovery during the waterflood and CO<sub>2</sub> miscible flood would occur through imbibition and diffusion mechanisms, rather than through pressure-driven displacement. This is a valid and very important point that should be recalled for researchers considering the use of oil in conformance-related core-scale experiments. Testing the chemical resistance of polymer gel systems in the presence of reservoir oil is important, but recovery factors and assessment of field-scale success should not be lightly upscaled from such experiments. Effects such as diffusion, imbibition, and water shielding are much more significant in core-scale experiments than on field scale, and direct application of experimental data may lead to an overestimation of oil recovery and an underestimation of the conformance issue at hand (Seright 1991).

In-Situ Imaging of Polymer Gel-CO2 Conformance in Fractured Cores. In-situ imaging was in some publications applied in addition to (or instead of) pressure measurements to distinguish blocking mechanisms, separate matrix and fracture production, and correctly establish the influence of conformance control. Al-Ali et al. (2013) and Xiao et al. (2016) used computed tomography imaging to visualize CC/AP gel treatments and subsequent CO<sub>2</sub> flooding in fractured cores. Both papers focused mainly on recovery; hence, differential pressures and RRFs are not reported. Al-Ali et al. used limestone where the fracture permeability was approximately 30 times higher than the matrix and performed experiments with and without the presence of oil. Polymer gel was injected in both the gelant and preformed state, where a shut-in period was allowed after gelant injection for in-situ aging. During preformed polymer gel injection into a 100% oil-saturated core, computed tomography imaging showed a saturation change in the matrix. The authors proposed gel leakoff into the matrix, but we propose that this could rather be water leakoff from preformed polymer gel, which is expected during propagation through a fracture (Seright 2003). Computed tomography imaging relies on density differences and would not be able to differentiate between polymer gel with >99% water content and water leakoff. A lower volume of polymer gel would remain in the fracture due to either mechanism-gel or water leakoff into the matrix. However, with water leakoff, a more concentrated gel would be present in the fracture to contribute to conformance control. Gel production was observed during the first pore volume of  $CO_2$  injected in this experiment. The polymer concentration was thereafter increased from HPAM 3,000 to 7,500 ppm. Less leakoff was observed during the injection of higher concentration preformed polymer gel, which largely remained in the fracture to contribute to conformance control. Al-Ali et al. found that the degree to which gel filled the fracture significantly influenced CO<sub>2</sub> displacement: CO<sub>2</sub> diffused into the matrix in narrow segments of the fracture, and the effect of the fracture on CO<sub>2</sub> channeling was diminished. Wider segments of the fracture, however, experienced severe CO<sub>2</sub> channeling, leaving matrix oil unswept.

Wassmuth et al. (2005) and Brattekås et al. (2013) used magnetic resonance imaging to visualize polymer gel impact on  $CO_2$  displacements in fractured limestone. Wassmuth et al. (2005) found that polymer gel efficiently diverted flow from the fracture and allowed oil to be produced from the matrix during  $CO_2$  flooding. Although the fracture was not completely filled by gel—and the effective fracture permeability was higher than matrix permeability—miscible  $CO_2$  flooding could achieve similar oil recoveries in polymer gel-treated fractured cores and nonfractured cores. Polymer gel placement was the most effective means of  $CO_2$  conformance control in fractured cores, compared twith foam and foamed polymer gel. Brattekås et al. (2013) injected preformed polymer gel into a fractured and oil-wet core and subsequently injected weak  $CO_2$  foam. Their system allowed for chase-fluid injection directly into the matrix. Thus, this is also a hybrid system where pressures and breakthrough properties depend on the properties of both the polymer gel and the matrix. They found that foam swept the matrix more efficiently after polymer gel was placed in the fracture.

The few available papers utilizing polymer gel for fracture blocking in  $CO_2$  floods reflect a significant span in both parameters investigated and methodologies used. Due to the use of hybrid matrix/fracture core systems and imaging rather than pressure measurements to assess flow patterns, deeper comparison between the studies is not straightforward. We find that there is currently a gap in the existing literature showing polymer gel efficiency in the treatment of  $CO_2$  channeling and propose a systematic approach in new experiments, where the influence of different parameters is assessed.

#### **Concluding Remarks**

This paper intended to describe previous experimental work where polymer gels were applied for  $CO_2$  conformance control in porous or fractured media on the laboratory scale and define possible gaps in the research field. Polymer gel stability and compatibility with  $CO_2$  remain important and have been covered in previous reviews, while we have focused on polymer gel injectivity and subsequent resistance to flow, which has received less focus.

Optimally, this review would have allowed us to answer the following important questions: Can polymer gel efficiently block the flow of  $CO_2$ ? Will polymer gel block  $CO_2$  flow substantially different from water flow? Although these are seemingly straightforward questions, our review shows that a complicated answer is likely demanded: It depends on a number of parameters.

Laboratory experiments agree that polymer gel is able to block or significantly reduce  $CO_2$  flow, although the efficiency and duration of the treatment vary. Gel-blocking efficiency seems to be unambiguously connected to polymer gel type and concentration, as well as the gel state during placement. The following parameters may play a role, although their importance is not yet disclosed:

- 1. *Miscibility:* Unlike water, CO<sub>2</sub> can develop miscibility with the matrix oil instantaneously (first contact miscibility) or with time (multicontact miscibility). Miscible CO<sub>2</sub> floods may behave significantly different from immiscible floods in terms of their ability to bypass fractures without the aid of polymer gel.
- 2. *The state of injected CO*<sub>2</sub>: The difference between reviewed papers cannot be ascribed to CO<sub>2</sub> phase due to a number of other variables.
  - Pressure and temperature will significantly influence the viscosity and density of the injected CO<sub>2</sub>, while water is not significantly compressible in liquid condition (and is liquid for ambient as well as most practical reservoir conditions). Experimental conditions may therefore be more influential during CO<sub>2</sub> chase floods than in previously performed water chase floods.
  - The CO<sub>2</sub> phase at experimental conditions will directly influence the acidity of the brine/CO<sub>2</sub> combination, which will again affect the stability of different polymer gel systems. Although gel stability was not the focus of this paper, the parameter's importance is acknowledged, especially for seal leakage remediation.
- 3. *The properties of the matrix*: We note that RRF values vary significantly in matrix studies and are most likely field specific, polymer gel specific, and/or condition specific; hence, current literature does not give grounds to approximate RRF values based on experience.
  - Studies including RRF indicate that polymer gel induces a "disproportionate permeability effect" in the presence of water and CO<sub>2</sub> that may be similar to previously investigated multiphase systems (water/oil) in most consolidated systems, where polymer gel reduces the flow of water notably more than that of CO<sub>2</sub>. Opposite results were, however, achieved in unconsolidated systems, which should be further investigated. Surface wettability (which ties into several bullet points) is another unknown factor, probably influencing the ability of polymer gel to reduce CO<sub>2</sub> flow in both matrix and fracture systems.
  - Core mineralogy may influence polymer gel formation (during or after gelant injection) and stability. Sandstone formations are preferred for CO<sub>2</sub> storage, while widespread carbonate formations are candidates for CO<sub>2</sub> EOR. Both core materials have been used for experimental research, but only in a few studies with varying experimental conditions. A difference has not yet been captured but should be considered in future studies, especially taking acidification and potential dissolution of the carbonate matrix into account.
- 4. Fractures: This review identifies a gap in the research related to CO<sub>2</sub> conformance in fractured media. Fractures have a known impact on CO<sub>2</sub> displacement efficiency, and this review presents evidence that different polymer gels may reduce fracture channeling. However, experimental studies applying polymer gels to reduce CO<sub>2</sub> flow in fractures are limited relative to frequently reported channeling issues during CO<sub>2</sub>EOR on the field scale.
- 5. *Fracture aperture:* The inability of polymer gel to block large fractures remains a significant challenge in CO<sub>2</sub> conformance control, yet controlled studies testing the influence of fracture width are currently not reported. This challenge may be similar in CO<sub>2</sub> and waterfloods, although reports targeting this obstacle are largely missing, and the mechanistic behavior of CO<sub>2</sub> displacing or breaking polymer gel is not yet disclosed.
- 6. *The state of injected gel:* The propagation properties of CC/AP gel have been thoroughly mapped, but for several new polymer gel systems (including PPGs), propagation properties in fractures have not been characterized.
- 7. Further work is needed to benchmark and develop CO<sub>2</sub> conformance control by polymer gel. For each gel system, we recommend reporting repeated and trustworthy baselines to which parameter sensitivities may later be compared. We find that polymer gel properties are detailed and well controlled in studies proposing new gel systems, but core-scale experiments performed to evaluate their efficiency in CO<sub>2</sub> conformance often lack the same degree of detail and control. We strongly urge future experimental studies to report the measured data (including pressure development with time during injection of a known phase at a known rate and volume) in addition to detailed experimental conditions and core properties. Rigorous reporting of measured data enables improved comparison between different gel systems, enefitting both researchers and operators.

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Fig. A-1—Polymer gel has been implemented for  $CO_2$  conformance control (1) and researched as a means to remediate wellbore (2) or seal (3) leakage, or  $CO_2$  leakage to and in an over-lying aquifer (4).

Field (Location)	ocation) Polymer gel treatment		Outcome
Enick and Olsen (2012); Moffit	t and Zornes (1992); Woods et al. (1986)		
Lick Creek field (Arkansas, USA)	HPAM/Cr(VI)	1978	Gelation occurred, but conformance control only efficient for a few WAG cycles. Gel may have been unable to withstand acidic environment.
	in-situ polymerized acrylamide monomer	1984	Gels formed in situ
Friedmann et al. (1997); Hild a	nd Wackowski (1999); Sydansk and Southwell	(2000)	
Rangely Weber sand unit (Colorado, USA)	High Mw HPAM/ Cr(III)-acetate	1994–1997	Gel used to treat high-permeable streaks and fractures. Total pattern $CO_2$ injection increased and $CO_2$ production decreased
			The gel system was resistant to the low pH environment associated with $CO_2$ flooding and, hence, effective
Borling (1994)			
Wertz field (Wyoming, USA)	High Mw HPAM/ Cr(III)-acetate		Pattern life extended by nearly two years
Larkin and Creel (2008); Smith	n et al. (2006)		
Anton Irish field (Texas, USA)	HPAM solution	1991	
	in-situ polymerized acrylamide monomer	1993	Effective for 1-2 years

Table A-1—Outcome of gel treatments for CO<sub>2</sub> conformance control on the field scale and references from which the information is collected.

Field (Location)	Polymer gel treatment	When	Outcome
	High Mw HPAM-Cr(III)-proprionate + foamed cement	2003	still effective after 3.5 years
	Improved formulation	2005	Increase in oil production, decrease in gas production
	Preformed particle gels (PPG)	2007	no significant change in injectivity
Larkin and Creel (2008); Pipes	and Schoeling (2014)		
SACROC (Permian Basin, USA)	PPG (superabsorbent crystallized copolymer)	2007	Improvements in sustained conformance control (9 treatments) or little change (2 treatments). One failed treatment due to quick polymer swelling.
	High Mw HPAM/ Cr(III)-acetate	2010- 2014	Gel in CO <sub>2</sub> flooded area (29 treatments) and in another area before CO <sub>2</sub> flooding (30 treatments). Oil production peak faster and decline slower if gel treatment implemented before CO <sub>2</sub> , at producible GOR. Confirmed interwell communication by polymer presence in offset wells.
Karaoguz et al. (2007); Sahin e	et al. (2012); Topguder (2010); Topgüder (1999)		
Bat Raman field (Turkey)	Low Mw HPAM-Cr(III)-acetate	2002	Near well treatment. Gel plugged high-permeability fracture and cutoff well communication. Oil production increased.
	High Mw HPAM-Cr(III)-acetate	2004	Deep formation treatment. Oil production increased and gas production decreased for about one year. Reduced CO <sub>2</sub> injectivity for extended period of time.
Creel et al. (2001); Honnert et a	al. (2006)		
Permian's Slaughter field (Texas, USA)	In situ polymerized acrylamide polymer	2000–2005	Oil production maintained, or oil production decline reduced. Gas production and injection reduced.
Cain (2010); Enick and Olsen (	2012)		
Brookhaven field	High Mw HPAM with unspecified organic crosslinker	2008	Injectivity decreased in three of the four injectors. Other effects not easily distinguishable: gel volumes may have been too small.
	HPAM concentration of 0.3-3-0.9 wt %	2009	

Table A-1 (continued)—Outcome of gel treatments for CO<sub>2</sub> conformance control on the field scale and references from which the information is collected.

		Crosslinked PAM			
Martin and Kovarik (1987)	Polyacrylamide/Chromium	Monomer	Xanthan/ Chromium		
Initial brine injection	5.99	5.59	5.48		
1st CO <sub>2</sub> cycle	6.29	1.28	14.49		
1st brine cycle	2.45	1.48	2.10		
2nd CO <sub>2</sub> cycle	2.03	1.18	6.49		
2nd brine cycle	3.09	1.22	1.59		
3rd CO <sub>2</sub> cycle	1.00	1.00	6.33		
3rd brine cycle	1.00	1.36	1.00		
Martin et al. (1988)	Xanthan/ Chromium	Low conc. crosslinker	High conc. crosslinker	2.5% FLOPERM 325	
100% Sw				Reservoir core	
Initial brine injection				34.48	
1st CO <sub>2</sub> cycle	2.42	5.08	55.56	71.43	
1st brine cycle	3.91	4.07	166.67	3.01	

Table A-2—Reported or calculated RRF values used as basis for Figs. 2 and 3.

Martin and Kovarik (1987)	Polyacrylamide/Chromium	Crosslinked PAM	Yanthan/ Chromium		
2nd CO, avelo	2.62	2 21	17.96	02.22	
	2.02	2.31	17.00	05.55	
	3.17	0.33	63.33	3.53	
Seright (1995)	1.91 Xanthan/ Chromium	3.24 Colloidal silica	16.67 HPAM/ Chromium (P =	58.82 HPAM/ Chromium (P = 1500 psi)	
Initial brine injection		32.000	272.000	4.970	
1st CO <sub>2</sub> cycle	12	400	500	148	
1st brine cycle	23	3,800	1,720	472	
2nd CO <sub>2</sub>		380	50	64	
2nd brine cycle		2,600	549	177	
3rd CO <sub>2</sub>		290	13	34	
3rd brine cycle		1,800	131	94	
Raje et al. (1996)					
single-phase CO <sub>2</sub>	4.5	4.8	8.0	15.5	
Taabbodi and Asghari (2006)	AF935 (no oil)	AF935 (oil)	AF245S (oil)	AF935 (sodium lactate)	
Initial brine injection	-	224	164	16,000	
1st CO <sub>2</sub>	17,920	4,050	6,447	5,200	
1st brine	4,258	163	120	5,000	
2nd CO <sub>2</sub>	20,160	1,572	4,900	5,100	
2nd brine	2,599	122	115	7,000	
3rd CO <sub>2</sub>	15,680	1,279	4,623	7,000	
3rd brine	1,740	111	114	8,000	
4th CO <sub>2</sub>	14,560	1,012	4,573	8,000	
* brine and CO <sub>2</sub> injected at c	lifferent rates				
Syed et al. (2014)	K before	K after	Calculated RRF		
single-phase CO <sub>2</sub>	2,171	0.0005	4,342,000		
	1,928	0.0015	1,285,333		
	2,147	235	9		
	1,936	66	29		
Durucan et al. (2016)	K before	K after	Calculated RRF		
single-phase CO <sub>2</sub>					
Guilting carbonate	670.25	1.03	651		
Doddington sandstone	578.78	0.03	19,293		
Mosleh et al. (2016)	K before	K after	Calculated RRF		
single-phase CO <sub>2</sub>	352	0.02	17,600		
	450	0.6	750		
	619	8	77		
	2,180	6	363		
	1,928	0.0015	1,285,333		
Sun et al. (2021)	107 mD	282 mD	350 mD	431 mD	1225 mD
1st CO <sub>2</sub>	4.37	3.85	2.98	2.78	1.19
1st brine	82.43	70.31	50.51	49.02	5.37
2nd CO <sub>2</sub>	3.65	1.55	1.43	1.38	1.29
2nd brine	74.82	29.17	19.24	17.76	4.15

\*Small effect of flow rate measured in work: here averaged across flow rates.

Table A-2 (continued)—Reported or calculated RRF values used as basis for Figs. 2 and 3.