

# Research on a novel composite gel system for CO<sub>2</sub> breakthrough

Hou Yongli<sup>1</sup> and Yue Xiang'an<sup>2\*</sup>

<sup>1</sup> Production Optimization, China Oilfield Services Limited, Tianjin 300450, China

<sup>2</sup> Enhanced Oil Recovery Research Center, China University of Petroleum, Beijing 102249, China

© China University of Petroleum (Beijing) and Springer-Verlag Berlin Heidelberg 2010

**Abstract:** A composite gel was prepared for plugging CO<sub>2</sub> channeling, which is a serious problem for enhanced oil recovery with CO<sub>2</sub>. A composite gel which is one of the materials for successful control of CO<sub>2</sub> channeling during CO<sub>2</sub> injection process was studied in this paper. SEM and nano particle size analysis were used to describe this material's microstructure. Its effect on CO<sub>2</sub> channeling control was evaluated with core flow experiments. Both the rheological test and core plugging experiments indicated that both acrylamide monomer concentration and reaction pressure had positive influences on gel properties. The gel system with an acrylamide monomer concentration of 2% and 5% sodium silicate was proved to have excellent strength, elastic and plugging efficiency, which confirmed huge development potential and wide application of the composite gel system. The high-pressure acid environment arising from the CO<sub>2</sub> injection not only reacts with solid silicate to form silicic acid gel, but also facilitates efficient polymerization.

**Key words:** Enhanced oil recovery, CO<sub>2</sub>, channeling, composite gel, acrylamide monomer

## 1 Introduction

In field application, the viscosity of CO<sub>2</sub> is lower by more than an order of magnitude than that of either crude oil or the brine occupying the remainder of the pore space of the reservoir rock. Additionally, large-scale reservoir heterogeneities, such as fractures, channels, or high-permeability streaks always exist in reservoirs. So gravity segregation and viscous fingering usually causes early breakthrough of injected CO<sub>2</sub> and thus reduces oil recovery (Gozalpour, 2005).

Many methods have been proposed for mobility control during CO<sub>2</sub> flooding: the water-alternating-gas (WAG) process (Kulkarni and Rao, 2005; Nezhad et al, 2006), the use of foam to reduce gas mobility (Xie et al, 1990; Gauglitz et al, 2002; Grigg et al, 2002), direct thickening of the CO<sub>2</sub> (Enick et al, 2000; Xu and Enick, 2001), chemical gel (Martin and Kovarik, 1987; Seright, 2007), carbonate precipitation (Aminian et al, 1989; Zhu and Raible, 1994), gel foam (Yang et al, 2003), etc. However, these methods have their own limitations in the field application, such as technical feasibility, application efficiency, environmental requirements, safety, etc (Moritis, 1995). So it is particularly necessary in petroleum industry to develop an environmental-friendly, highly-effective CO<sub>2</sub> plugging system.

Chemical gels are introduced to reduce or block

channeling through the fractures or high permeability layers in oil reservoirs. These divert fluid flow to lower permeability layers and improve the oil recovery (Asghari and Taabbodi, 2004). However, the strength and stability of conventional gel systems still needed to be improved, especially in the complicated environment of CO<sub>2</sub> injection (Orr et al, 1982). Consequently, several composite gel systems were developed. Organic gel systems would present better mechanical performance (Maiti et al, 2002), swelling properties, and thermal stability (Yoon et al, 2002) after the addition of inorganic materials. Messersmith et al (1997) obtained a composite gel which gelled in a suspension of montmorillonite after the addition of *n*-isopropyl acrylamide and methylenebisacrylamide. Haraguchi and Li (2006) prepared hydrogels with improved mechanical properties starting from AAm-based monomers together with Laponite (a synthetic clay product) as a physical cross-linker, replacing the traditional chemical cross-linkers. Song et al (2006) added SiO<sub>2</sub> nano-particles in a solution of N-N-methylenebisacrylamide and acrylamide, then ultrasonically treated the solution and added an initiator and then a catalyst, forming a composite gel in a nitrogen atmosphere. Jiang et al (2008) proposed a novel bio-degradable composite gel in aqueous solution using CaCl<sub>2</sub> as crosslinking agent and konjac glucomannan (a natural food additive) and sodium alginate as main materials. Wang et al (2005) formed a high-strength composite gel by adding inorganic rigid fillers and crosslinking agent successively into a polymer solution with the fixed pH value.

\*Corresponding author. email: yxa@cup.edu.cn

Received October 16, 2008

A new kind of organic-inorganic composite gel is proposed in this paper which is endowed with dual excellent characteristics of polymer gels and inorganic gels, such as resistance to high temperature and pressure, and high elasticity. The sodium silicate solution and organic polymer solution are blended, and then gelled at the high-pressure acid environment formed by CO<sub>2</sub>. Overcoming the collapsibility of silicic acid gel and poor efficiency in plugging macrospores of polymer gels, the new gel system has good potential for plugging gas channeling.

## 2 Experimental

### 2.1 Experimental materials

Sodium silicate, provided by the Hebei Fine Chemistry Company, has a density of 1.36 g/cm<sup>3</sup>, modulus of 2.8-3.2, and mass concentration of 40%. Acrylamide monomer, potassium persulfate, and N-N-methylenebisacrylamide are all commercial analytical grade (Beijing Chemical Reagents Company), which have the purities of 96%, 99.5%, and 99%, respectively. Artificial cores were constructed by packing inorganic adhesive material, clay mineral, and outcrop sand from an outcrop at Qinhuangdao into steel moulds (80cm×80cm×20cm). The water used in all experiments is distilled water. CO<sub>2</sub> and N<sub>2</sub>, provided by Beijing Haipu Company, both have the purity of 99.99%.

### 2.2 Apparatus

A high-pressure reactor made by Jiangsu Hai'an Instrument was used to control conditions for gellation. A set of core flow test equipment made also by Jiangsu Hai'an Instrument was used to determine the permeability of sand packs and evaluate plugging efficiency of gel systems and foam stability in porous media. A HAAK RS600 rheometer made in German was used to perform rheological property measurements. A KQ3200 ultrasonic cleaning machine was used to cause the shedding of inorganic particles from the polymer network, and the particle size was measured with a laser particle size analyzer (Malvern instruments, UK). The microstructure of surfaces of the composite gel was observed with a field emission gun environmental scanning electron microscope (FEG-ESEM) (made in the Netherlands).

### 2.3 Experimental procedures

#### 2.3.1 Sample preparation

A sodium silicate mother liquor of 12.5 grams was added to 87.5 milliliters of distilled water. After stirring evenly, acrylamide monomer, initiator, and crosslinking agent were added to the solution which was stirred until the solution was clear. Twenty milliliters of mixed solution were charged into the reaction vessel, and the temperature-controlling system of the reactor was turned on. CO<sub>2</sub> was then injected into the reaction vessel through a piston-cylinder container until the inward pressure reached the fixed point. The reaction vessel was then sealed and stirred for about 20 minutes. After standing at 45 °C for about 12 hours, the sample was taken out. The above laboratory procedure was repeated at a series

of reaction pressures and at different amounts of acrylamide monomer, as shown in Table 1.

**Table 1** Preparation parameters of composite gel samples

Sample	Sodium silicate concentration, wt%	Acrylamide monomer, wt%	Reaction pressure MPa
1#	5.0	2.0	6
2#	5.0	2.0	4
3#	5.0	1.5	6
4#	5.0	1.5	4

#### 2.3.2 Determination of particle size

Twenty milliliters of sample 1# were put into a flask with distilled water and ultrasonically treated for 2, 4, and 16 minutes, respectively. The supernatant liquid was placed in the particle size analyzer for determining the particle distribution. The experiment temperature was kept at 45 °C.

#### 2.3.3 Rheological experiment

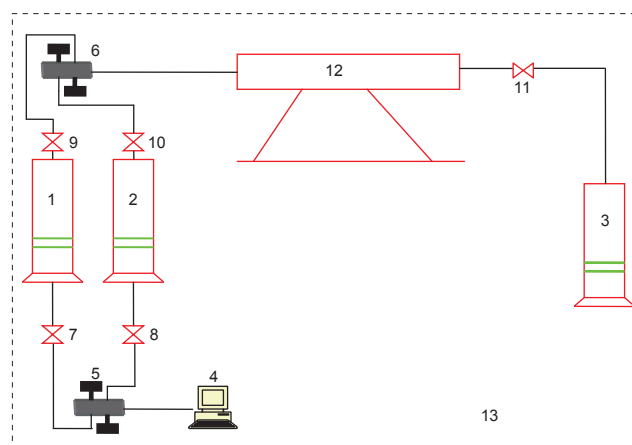
Yield pressure and creep recoverability of four gel samples were measured with the HAAK RS600 rheometer.

#### 2.3.4 Environmental scanning electron microscopy

Microstructure and surface characteristics of sample 1# were examined with the FEG-ESEM.

#### 2.3.5 Plugging effect in porous media

Cores were prepared and their diameters, lengths and weights were measured. After being evacuated and water-saturated, the wet weights, permeabilities to gas and water of the cores were tested. When the experimental apparatus was prepared, 0.4 pore volume of composite gel solution and 0.6 pore volume of CO<sub>2</sub> were injected into the cores and the reaction pressure was adjusted to 4 or 6 MPa. Then permeabilities to gas and water were measured again after gelling for 12 hours. Fig. 1 shows the experimental equipment in which the composite gel was formed.



**Fig. 1** Core flow experimental equipment

1, 2, 3: Piston containers for blocking agent, gas, and back-up pressure; 4: Constant-flow pump; 5-11: Valves; 12: Core holder; 13: Thermostat

### 3 Experimental results and discussion

#### 3.1 Microstructure of the composite gel and its gellation mechanism

The gelation mechanism can be explained as follows: The cross-linking polymerization system comprising acrylamide monomer and N, N-methylenediacylamide. The existence of amide groups in the acrylamide monomer allows the



The three-dimensional structure of silicon-oxygen chains selectively recognizes the polar groups in acrylamide monomer (AM). It is exactly this characteristic that makes the three-dimensional structure or silicic acid gel particles distribute regularly in the organogel skeleton and restricts the movement of silicic acid gel. Besides this, silicic acid gel particles inlaid in the skeleton influence the deformation of gel and thus enhance the stability and strength of gel to different extents (Wang et al, 2005). The more sodium silicate is added, the more networks will be formed and the stronger the gel is. The more AM is added, the stronger the gel elasticity becomes.

Observed by the FEG-ESEM, the composite comprising the silicic acid gel and polymer gel had excellent fluidity and viscoelasticity. A deformed and folded surface is shown in Fig. 2. The main part of gel surface structure was the network formed by polymer gel, on which silicic acid gel particles with different sizes were inlaid, as shown in Fig. 3.

#### 3.2 Gel particle size analysis

The particle size distribution experiments were designed for measuring the particle size of silicic acid gel. Through dehydration, the silicic acid gel particles are more outstanding to observe in the ESEM image. Fig. 4 illustrates the structure

formation of hydrogen bonds among chain segments, which thus strengthens bonding force among them.

A three-dimensional structure is formed as the basic skeleton of the gel after the combination of chain segments. Sodium silicate, a supplement to the system, is transformed into silicic acid gel with the condensation product of silicon-oxygen chains in the acid environment of CO<sub>2</sub> solution. The molecular structure of silicon-oxygen chains can be illustrated as follows:

of the dehydrated gel. It can be seen that the dehydrated gel is composed of densely packed particles bonded with each other. The particle diameters of gel, measured with the nano particle size analyzer, varied from 327.5 to 854.7 nm, which

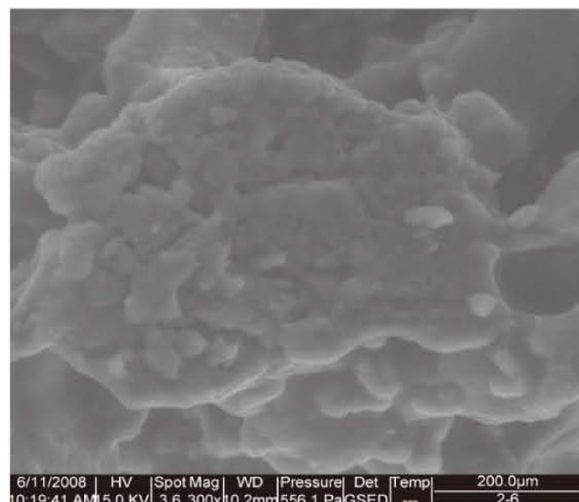


Fig. 3 ESEM image of the composite gel

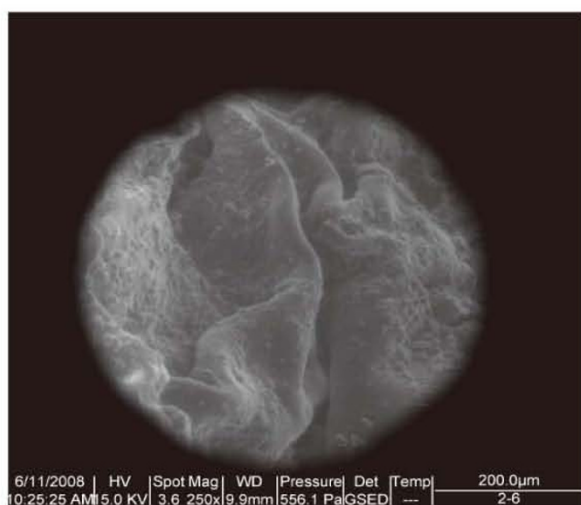


Fig. 2 ESEM image of the surface of the composite gel

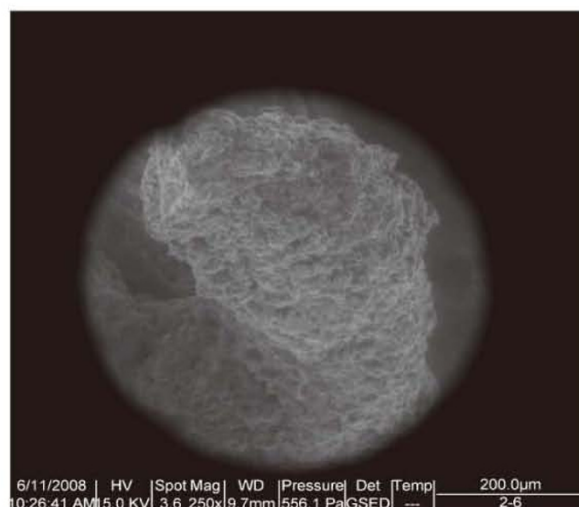


Fig. 4 The microstructure of the dehydrated gel



ensured that these particles could be easily attached to the polymer fiber skeleton and thus strengthened the gel system (Zhao, 2009).

With an increase in ultrasonic treatment time, the gel particle size showed a nonlinear decrease (see Fig. 5). Silicic acid gel particles, regularly inlaid on the network formed by polymer gel, started shedding in the process of ultrasonic treatment. With the treatment time prolonged, more and more particles were shed.

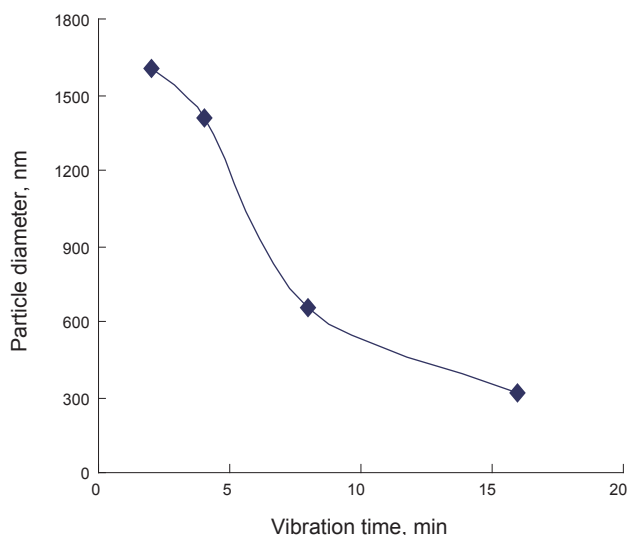


Fig. 5 The influence of vibration time on particle diameter

### 3.3 Rheological properties of the composite gel

In the experiments, two methods were used to evaluate the rheological properties of the gel system. One was creep and recovery experiments which measured the creep compliance of the gel system. The other was the determination of the dynamic yield stress which measured yield stress to assess the gel strength.

#### 3.3.1 Yield stress of the composite gel system

The yield stress refers to the minimum critical external force when materials begin to flow when the external force is higher than internal structural force. If the external force is lower than the yield stress, materials usually show elastic behavior like solid materials. Otherwise, materials exhibit deformation and elastic failure.

For the composite gel, the flexible chains of polymer gel showed extensional deformation at first under external force, but silicic acid gel particles embedded in the structure hindered the extensional deformation and resisted pressure, which ensured the strength of the gel system. The introduction of sodium silicate greatly improved the performance-price ratio of the gel, which made this system practical and economic for plugging CO<sub>2</sub> channeling. When the experimental temperature was at 45 °C and the vibration frequency was 0.1 Hz, the range of yield stress for four different samples fluctuated from 16,010 to 17,630 Pa, which is much higher than that of a conventional gel system.

#### 3.3.2 Creep-recovery properties of the composite system

Materials will creep under certain external stress and will recover in an opposite direction when the stress is removed. Besides this, the strain of materials in the recovery process decreases with time. This phenomenon is referred to as creep-recovery behavior. The creep-recovery capacity of the gel, indicating the viscoelastic effect of polymer solution, reflects its resistance to internal slip deformation. When a gel is studied in its linear viscoelastic region, its creep curve can be divided into a recoverable strain part and an unrecoverable strain part. Fig. 6 showed the creep-recovery curves as well as their comparisons for three different samples. As was seen in Fig. 6, the larger the concentration of acrylamide monomer and the higher the reaction pressure, the higher the creep compliance of the gel system. So it could be concluded that high pressure conditions were beneficial to polymerization of acrylamide monomer and that high concentration of acrylamide monomer could strengthen the affinity of molecular chains.

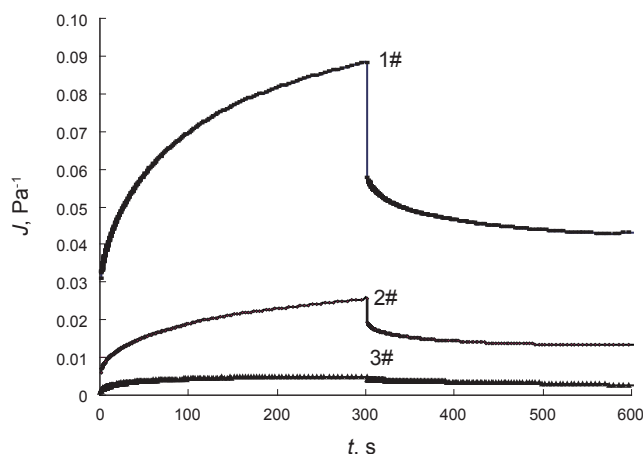


Fig. 6 The creep-recovery properties of three different gel systems

### 3.4 Core plugging experiments

According to above experiments and oilfield conditions, the composite gel systems with the acrylamide monomer concentration of 1.5% or 2%, reaction pressure of 4 or 6 MPa, were chosen as experimental parameters in the core plugging experiments. The gel performance was evaluated mainly by plugging strength in porous media, which was denoted by plugging rate  $S$  and residual resistance factor  $F_{RR}$ . Table 2 and Table 3 showed the core parameters and experimental results. The plugging rate and residual resistance factor were calculated as follows:

$$S = \frac{K_0 - K_1}{K_1} \quad (1)$$

$$F_{RR} = \frac{K_0}{K_1} \quad (2)$$

where  $K_0$  is the permeability to water before plugging;  $K_1$  is the permeability to water after plugging.

**Table 2** Physical properties of cores used

Core	Length cm	Diameter cm	Cross-sectional area, m <sup>2</sup>	Volume cm <sup>3</sup>	Pore volume cm <sup>3</sup>	Porosity %
FH 1-1	8.826	2.556	5.13	45.26	10.83	23.92
FH 1-5	8.736	2.53	5.02	43.90	9.92	22.59
FH 1-6	8.662	2.534	5.04	43.66	10.49	24.03
HF 1-7	8.608	2.532	5.03	43.32	13.26	30.62
HF 1-9	8.668	2.55	5.10	44.25	13.55	30.62
HF 1-10	8.607	2.532	5.03	43.28	11.80	27.27

As was indicated in Table 3, the composite gel had a favorable breakthrough pressure gradient which was not lower than 18.39 MPa/m. So it was fairly applicable in actual field plugging if the length of the core was converted to the actual well spacing. The constant-flow pump, used in the experiments as a displacement power source, has a maximum pressure endurance of 20 MPa. In the experiments, the displacement pressure sometimes got close to the maximum pressure endurance, especially when back pressure was used. In that case, the final pressure shown in the form of italics in Table 3, was chosen as equilibrium pressure to calculate the permeabilities, plugging rate, and residual resistance

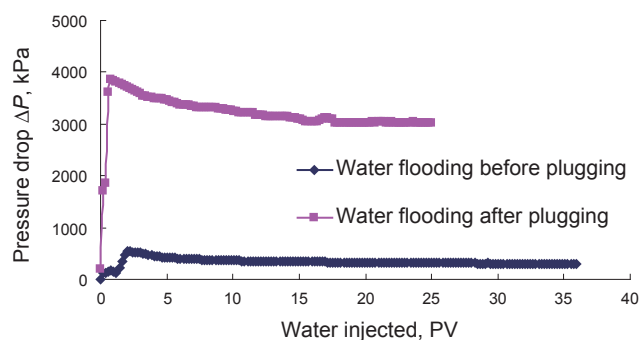
**Table 3** The results of core plugging experiments

Core	AM concentration wt%	Reaction pressure MPa	$K_0$ mD	$K_1$ mD	$S$	$F_{RR}$	Breakthrough pressure gradient MPa/m
FH 1-1	2.0	4	53.97	2.41	0.96	22.38	29.53
FH 1-5	1.5	4	19.23	7.23	0.62	2.66	18.39
FH 1-6	1.5	4	18.95	1.32	0.93	14.37	44.56
FH 1-7	1.5	4	161.27	36.12	0.78	4.47	14.86
FH 1-9	2.0	6	50.38	0.02	0.99	2279.09	147.70
FH 1-10*	2.0	6	34.10	0.02	0.99	1461.73	141.95
FH 1-10	2.0	6	34.10	0.02	0.99	2162.55	210.02

Notes: \* denotes the introduction of back-up pressure in the experiments

factor for the convenience of comparison. Fig. 7 showed the variation in the pressuredrop across the core before and after plugging by sample 1#.

Experimental results indicated that both the concentration of acrylamide monomer and reaction pressure had important influence on plugging effects. The higher the acrylamide monomer concentration and the higher the reaction pressure, the better the plugging effect. When the concentration of acrylamide monomer in the gel system was kept at 1.5%, the plugging effect changed irregularly. So it was concluded that the performance stability of the composite gel formed at this concentration needed to be increased. When the concentration of acrylamide monomer was increased to 2%, the gel system showed excellent plugging strength and stability, the plugging rate of all experiments was above 95%. Additionally, the plugging effect of the gel system was improved with the increase in reaction pressure, which was consistent with the rheological experiments. Therefore, the reaction pressure had a positive influence on gel performance. Taking all the above into account, the gel system had excellent toughness and pressure-resistance, which was qualified for plugging viscous fingering or channeling of CO<sub>2</sub>. The back pressure was used to simulate reservoir pressure conditions and avoid core structure failure. It was found that the plugging rate could be increased to 99% or above when the back pressure was applied, which confirmed the stability of the composite gel in reservoir conditions.

**Fig. 7** The variation in the pressure drop across the core

In conclusion, the system had excellent plugging performance and good potential for field applications.

## 4 Conclusions

1) The gel strength was greatly enhanced with nanoscale inorganic particles efficiently embedded in the fiber network of polymer gel. The composite gel system possessed strong elasticity and high deformation capacity when the acrylamide monomer concentration was 2% and reaction pressure was 6 MPa.

2) The high-pressure acid environment generated by CO<sub>2</sub> not only accelerated the gel formation, but also made the network of the organic system swell, thus improving

the viscoelasticity of the composite gel. The gel system had excellent plugging effect which could reach 95% or above.

3) The composite gel system flowed freely and could be injected into the formation easily. Additionally, it was a new type of pollution-free gas plugging system, which has good potential for oilfield applications.

## References

- Aminian K, Ameri S, Cunningham L E, et al. CO<sub>2</sub> mobility control by carbonate precipitation: A modeling study. Paper SPE 19321 presented at SPE Eastern Regional Meeting, 24-27 October 1989, Morgantown, West Virginia
- Asghari K and Taabbodi L. Laboratory investigation of in-depth gel placement for carbon dioxide flooding in carbonate porous media. Paper SPE 90633 presented at SPE Annual Technical Conference and Exhibition, 26-29 September 2004, Houston, Texas
- Enick R M, Beckman E J, Shi C M, et al. Direct thickeners for CO<sub>2</sub>. Paper SPE 59325 presented at SPE/DOE Improved Oil Recovery Symposium, 3-5 April 2000, Tulsa, Oklahoma
- Gauglitz P A, Friedmann F, Kam S I, et al. Foam generation in porous media. Paper SPE 75177 presented at SPE/DOE Improved Oil Recovery Symposium, 13-17 April 2002, Tulsa, Oklahoma; also published at Chemical Engineering Science. 2002. 57(19): 4037-4052
- Gozalpour F, Ren S R and Tohidi B. CO<sub>2</sub> EOR and storage in oil reservoirs. Oil and Gas Science and Technology. 2005. 60(3): 537-546
- Grigg R B, Tsau J S and Martin D F. Cost reduction and injectivity improvements for CO<sub>2</sub> foams for mobility control. Paper SPE 75178 presented at SPE/DOE Improved Oil Recovery Symposium, 13-17 April 2002, Tulsa, Oklahoma
- Haraguchi K and Li H J. Mechanical properties and structure of polymer-clay nanocomposite gels with high clay content. Macromolecules. 2006. (39): 1898-1905
- Jiang P, Chen L G, Yuan X Q, et al. Study of preparation and swelling property of composite gel KGM/ALG. Journal of Anhui Agricultural Sciences. 2008. 36(31): 13504-13505 (in Chinese)
- Kulkarni M M and Rao D N. Experimental investigation of miscible and immiscible Water-Alternating-Gas (WAG) process performance. Journal of Petroleum Science and Engineering. 2005. 48: 1-20
- Maiti P, Yamada K, Okamoto M, et al. New poly(lactide)/layered silicate nanocomposites: Role of organoclays. Chemistry of Materials. 2002. 14 (11): 4654-4661
- Martin F D and Kovarik F S. Chemical gels for diverting CO<sub>2</sub>: Baseline experiments. Paper SPE 16728 presented at SPE Annual Technical Conference and Exhibition, 27-30 September 1987, Dallas, Texas
- Messersmith P B, Znidarsich F, Komarneni S, et al. Nanophase and nanocomposite materials II. Materials Research Society Symposium Proceedings, Materials Research Society, Pittsburgh, PA, 1997: 457-507
- Moritis G. Impact of production and development RD&D ranked. Oil and Gas Journal. 1995. 93(44): 37-39
- Nezhad S A T, Mojarad M R R, Paitakhti J S, et al. Experimental study on applicability of Water-Alternating-CO<sub>2</sub> injection in the secondary and tertiary recovery. Paper SPE 103988 presented at the First International Oil Conference and Exhibition, 31 August-2 September 2006, Cancun, Mexico
- Orr F M, Heller J P, Taber J J, et al. Carbon dioxide flooding for enhanced oil recovery: Promise and problems. Journal of the American Oil Chemists' Society. 1982. 59(10): 810-817
- Seright R S. Gels for conformance improvement in gas EOR. Flooding Syringe Pump Application Note AN8. 2007
- Song R, Xie Q L, He L H, et al. Synthesis and characterization polyacrylamide/silica composite hydrogel. Chinese Journal of Spectroscopy Laboratory. 2006. 23(3): 609-612 (in Chinese)
- Wang J J, Zhu J H, Xia S L, et al. Evaluation of the sealing ability of a new multi-function composite gel. Natural Gas Industry. 2005. 25(9): 101-103 (in Chinese)
- Xie S X, Yan W H and Han P H. Mobility control by foam in CO<sub>2</sub> flooding. Oilfield Chemistry. 1990. 7(3): 289-291 (in Chinese)
- Xu J H and Enick R M. Thickening carbon dioxide with the fluoroacrylate-styrene copolymer. Paper SPE 71497 presented at SPE Annual Technical Conference and Exhibition, 30 September-3 October 2001, New Orleans
- Yang B, Tang R Z, Luan C Z, et al. The technology of preventing CO<sub>2</sub> breakthrough and gravity segregation abroad. Fault-block Oil & Gas Field. 2003. 3(2): 64-66 (in Chinese)
- Yoon P J, Fornes T D and Paul D R. Thermal expansion behavior of nylon 6 nanocomposites. Polymer. 2002. (43): 6727-6741
- Zhao R B. Influence of carbon dioxide on the polymerization behavior of sodium silicate-acrylamide solution and products properties. Chemical Journal of Chinese Universities. 2009. 30(3): 596-600 (in Chinese)
- Zhu T and Raible C. Improved sweep efficiency by alcohol-induced salt precipitation. Paper SPE 27777 presented at SPE/DOE Improved Oil Recovery Symposium, 17-20 April 1994, Tulsa, Oklahoma

(Edited by Sun Yanhua)