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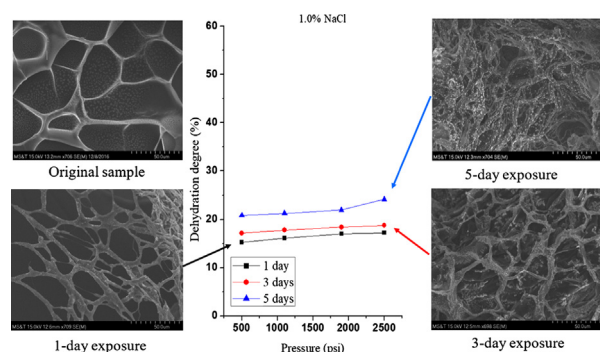
# Effect of supercritical CO<sub>2</sub> on the dehydration of polyacrylamide-based super-absorbent polymer used for water management

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## GRAPHICAL ABSTRACT



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## ABSTRACT

CO<sub>2</sub>-EOR (enhanced oil recovery) has been widely applied in the fields to improve oil recovery while sequestering CO<sub>2</sub> in reservoirs to reduce the greenhouse effect. Polyacrylamide-based super-absorbent polymer (PSAP) as a plugging agent has been used in CO<sub>2</sub>/water flooding fields to manage excess CO<sub>2</sub>/water production. However, the performance of PSAP under supercritical CO<sub>2</sub> conditions has not been systematically studied. A series of PSAP samples prepared in various salinity brines were evaluated under different pressures using newly designed high-pressure vessels to demonstrate the effect of CO<sub>2</sub> on PSAP. The swollen PSAP samples were kept in the high-pressure vessels and pressurized using CO<sub>2</sub> to various pressures. The vessels were kept vertically in a 65 °C oven for 1, 3, or 5 days. The PSAP samples before and after exposure to CO<sub>2</sub> were examined, and the free water left in the vessels was analyzed. It was observed that the swollen PSAP particle size became smaller due to significant dehydration. The dehydration became more severe with time. The scanning electron microscope (SEM) images showed that the PSAP network structure was more compacted with increased testing time. The PSAP's dehydration also increased with the increase of pressure and decreased with the increase of salinity. The re-swelling ratio was at least 91% of the original swelling ratio, and the swollen PSAP's strength decreased by 20% after exposure to CO<sub>2</sub>, which was caused by the loss of solid content, such as loosely bonded polymers. The major reason that caused the PSAP dehydration was the CO<sub>2</sub>-induced pH effect.

## 1. Introduction

The CO<sub>2</sub>-EOR technique has developed rapidly in recent decades

after the first introduction in 1952 by Brownscombe et al. [1]. CO<sub>2</sub>-EOR could not only improve oil recovery, but it could also sequester unwanted CO<sub>2</sub> in the reservoirs to reduce the greenhouse effect. Aycaguer

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### Nomenclature

AA	acrylic acid
AM	acrylamide
$D_{\text{loss}}$	PSAP's dehydration degree
PSAP	polyacrylamide-based super-absorbent polymer
SR	PSAP original swelling ratio, g/g

SRR	swelling ratio recovery, %
SEM	scanning electron microscope
$W_1$	dry PSAP weight, g
$W_2$	swollen PSAP weight, g
$W_3$	weight of PSAP after CO <sub>2</sub> flooding, g
$W_4$	weight of oven-dried PSAP after CO <sub>2</sub> flooding, g
$W_5$	weight of swollen oven-dried PSAP, g

et al. [2] estimated that the Permian Basin of West Texas has the capability to store 3 kg of CO<sub>2</sub> associated with 1 kg of oil production. Shaw and Bachu [3] utilized data from 8637 oil reservoirs in the Alberta reserves database and predicted that injecting 50% and 100% hydrocarbon pore volume of CO<sub>2</sub> could result in  $150 \times 10^6$  and  $442 \times 10^6$  m<sup>3</sup> oil production improvement while sequestering 127 and 591 MT of CO<sub>2</sub>. However, the CO<sub>2</sub> sequestration efficiency and oil recovery could be significantly decreased by early CO<sub>2</sub> breakthrough and excess CO<sub>2</sub> production, which is due to an unfavorable CO<sub>2</sub> injection profile, gravity override, and viscous fingering. Many methods have been reported to improve CO<sub>2</sub> sweep efficiency, such as alternating the injection of water and CO<sub>2</sub> (WAG) [4–7], CO<sub>2</sub> direct thickener [8–12], CO<sub>2</sub> foam [8,13–15], chemical gels, etc. The direct thickening method adds CO<sub>2</sub>-soluble polymer or small-molecule thickeners to supercritical CO<sub>2</sub> to increase CO<sub>2</sub> viscosity to reduce the fingering problem [16]. Heller et al. [17] identified that 18 polymers had a relatively high solubility in CO<sub>2</sub>, but the polymer could only slightly increase the CO<sub>2</sub> density. Shi et al. [10] synthesized a new CO<sub>2</sub>-soluble compound that could triple the CO<sub>2</sub> viscosity at 25 °C and 2400 psi. Farajzadeh et al. [18] conducted an evaluation of CO<sub>2</sub>-foam using sandstone cores. The computed tomography (CT) scanning of the cores showed that the foam could significantly improve the macro-sweep efficiency.

Some gel systems, such as polymer gel and preformed particle gel, have been evaluated and applied as plugging agents to control excess CO<sub>2</sub> production. Syed et al. [19] evaluated a polymer gel composed of AO-22 polymer from SNF company and Cr(III)-acetate crosslinker using high-permeability cores and fractured cores. The results revealed that this polymer gel could reduce permeability to CO<sub>2</sub> by 99% in high-permeability cores, and by 90% in fractured cores under 50 psi at 20–80 °C. Taabbodi and Asghari [20] examined a low-molecular-weight polyacrylamide gel (Alcoflood 254S-Cr(III)) and a high-molecular-weight polyacrylamide gel (Alcoflood 935-Cr(III)) using crushed carbonate porous media under 1200 psi at 40 °C. The results demonstrated that both gels could reduce permeability to water by > 90% and to CO<sub>2</sub> by > 99.7%. Seright [21] reported the disproportional permeability reduction behavior of Xanthan-Cr(III) polymer gel, resorcinol-formaldehyde gel, HPAM-Cr(III) gel, and colloidal silica gel in sandstone rocks under 900 and 1500 psi. The results showed that the resistance to water was higher than to CO<sub>2</sub>. Seright [21] also presented the disproportional permeability reduction for CO<sub>2</sub> and water of HPAM-Cr(III)-acetate polymer gel in polyethylene, sand pack, and fused silica. Martin and Kovarik [22] evaluated the polyacrylamide-Cr(III) gel and xanthan-Cr(III) gel under 1200 psi at 40 °C using sandstone cores. However, the results indicated that this polymer gel was only effective for two WAG cycles.

PSAP, a specialized polyacrylamide-based super-absorbent polymer, is synthesized on the surface facilities. Therefore, it has better control of gelation time and a higher resistance to shear degradation during pumping, chromatographic fractionation, and dilution by formation water [23–25]. PSAP has been applied in many water flooding fields to control water production [26]. Various models were designed to evaluate PSAP performance under water flooding conditions, but few studies have been reported for CO<sub>2</sub> flooding. Bai and Zhang [27] presented the PSAP behavior in open fracture models. The results showed that the PSAP, as a pore-filling material, propagated like a piston in a fracture and could reduce the permeability of the fractures with different widths

to the same level. Imqam et al. [28] conducted experiments using open conduits, which is defined as a large opening that naturally exists or is created by mineral dissolution or high injection pressure during the flooding process. Sun et al. [29] analyzed the PSAP behavior in improving area sweep efficiency using a transparent fractured sandstone model. Sang et al. [30] studied the sweep efficiency and oil recovery in parallel sand pack models. The results indicated that the PSAP could significantly improve sweep efficiency and recover more oil from low permeability zones. The improvement is more noticeable in the model with larger permeability contrast. Sun and Bai [31] conducted CO<sub>2</sub> flooding tests using a conduit model to study the dehydration of PSAP with various swelling degrees in CO<sub>2</sub> flooding. Wang et al. [32] simulated the plugging performance of PSAP in porous media by using a phenomenological model and analyzing the PSAP propagation rules. A few applications of PSAP in CO<sub>2</sub> flooding fields were reported, and the results were mixed. Larkin and Creel [33] presented that the PSAP could modify the injection profile and reduce excess CO<sub>2</sub> production in some wells in the Kelly-Synder field in Texas. Green et al. [34] reported that a PSAP treatment was performed to plug a high-permeability thief zone in the Cowden Unit in Texas, but the treatment was only effective for 5 months. Currently, no study has been conducted on PSAP's performance under high pressure and temperature.

In this paper, a series of tests were conducted using high-pressure vessels under various pressures and high temperatures. The objective was to systematically study how the properties and performance of PSAP with different swelling ratios changed with time under supercritical CO<sub>2</sub> conditions.

## 2. Materials

### 2.1. Polyacrylamide-based super-absorbent polymer

The polyacrylamide-based super-absorbent polymer is a commercial potassium salt of crosslinked polyacrylic acid/polyacrylamide copolymer. Before swelling, PSAP is a dry white powder with various particle sizes. The PSAP size used in this study was 20–30 mesh (0.595–0.841 mm). Due to the hydrogen bond with water molecules, PSAP can absorb a large amount of water when submerged in aqueous solutions. The amount of absorbed water was different when PSAP swelled in brines with various salinities. The swelling ratios of PSAP in different salinity brines are listed in Table 1.

### 2.2. Brine

Four solutions were used in this study: distilled water, 0.25, 1, and 10 wt% NaCl brine. PSAP has the highest swelling ratio in distilled water, and the swelling ratio decreases with the increase of brine

**Table 1**  
PSAP swelling ratio in brines with different salinity.

Sample ID	Brine salinity (wt.% NaCl)	Swelling ratio (g/g)
A	0 (Distilled water)	160.46
B	0.25	47.69
C	1	33.17
D	10	20.20

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