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Full Length Article

Ammonia-based ASP floods in carbonate cores containing gypsum

Himanshu Sharma, Upali Weerasooriya, Gary A. Pope, Kishore K. Mohanty*

The University of Texas at Austin, United States

HIGHLIGHTS

• An alkali was identified for ASP floods in carbonate cores containing gypsum.

• PHREEQC simulations correctly estimated gypsum dissolution.

• Effect of ammonia on surfactant adsorption was measured in ASP/SP floods.

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ABSTRACT

The amount of synthetic surfactants required for a surfactant flood can be minimized by the addition of an alkali. An alkali reduces surfactant adsorption on sandstone and carbonate rocks, and generates in-situ surfactant with acidic crude oils. Many reservoirs, especially carbonates, contain gypsum (or anhydrite), which is sparingly soluble in water. In such cases, a conventional alkali such as sodium carbonate cannot be added to alkaline-surfactant-polymer (ASP) formulations because it precipitates as CaCO₃ on interacting with gypsum (or anhydrite). In this study, we test ammonia as an alkali to perform ASP floods in carbonate cores containing gypsum. The concentration of calcium ions in the presence of gypsum when ammonia is used as alkali can be as high as 2000 ppm, depending on the brine salinity and composition. Therefore, surfactant and polymer selection study was performed to identify suitable candidates under high calcium concentrations. Oil recovery experiments were performed in carbonate cores containing gypsum, using ammonia as the alkali. PHREEQC, the USGS geochemical simulator, was used for reactive transport modeling and was found to be an effective tool for designing these corefloods. High pH propagation and good oil recovery was observed in the ASP coreflood performed in a carbonate core containing gypsum. Addition of sodium sulfate in injection brines decreased gypsum dissolution. Gypsum dissolution was also lower at higher temperatures and lower NaCl concentrations. The surfactant retention in the ASP coreflood using ammonia, however, was found to be about the same as that of the SP coreflood, even though a high pH propagation was observed during the ASP coreflood. A good agreement was observed between the measured concentration of the effluent ions from the corefloods and the PHREEQC simulations.

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1. Introduction

After primary and secondary recovery in an oil reservoir, a large amount of oil is left unrecovered due to trapping in the pores of the reservoir rock by capillary forces. Surfactants can mobilize this trapped oil by lowering the interfacial tension and polymers can provide mobility control and improve sweep efficiency. However, surfactants get retained in the reservoir due to adsorption on mineral surfaces and phase trapping [1]. Since a limited amount of surfactant can be used for an economical flood, the surfactant retention needs to be minimized. One way of achieving this objec-

* Corresponding author. *E-mail address: kishore.mohanty@engr.utexas.edu* (K.K. Mohanty). tive is by adding an alkali to the surfactant formulation to increase the pH, which reduces the adsorption of anionic surfactants by making sandstone and carbonate surfaces negatively charged [2,3]. An alkali also helps in minimizing requirements of synthetic surfactants by generating in-situ soap with acidic crude oils.

Many carbonate reservoirs contain either gypsum or anhydrite. Levitt et al. [4] discuss various challenges encountered in applying chemical EOR in carbonate reservoirs, especially in the presence of gypsum. Gypsum (CaSO₄·2H₂O) and anhydrite (CaSO₄) differ in the water of hydration. The transition from gypsum to anhydrite takes place at around 45 °C. Gypsum (or anhydrite depending on the temperature, but for convenience we refer to gypsum unless we are describing a specific instance of anhydrite) is commonly present in carbonate reservoirs, especially in dolomite formations







Nomenclature			
ASP CaCO ₃ CaSO ₄ CaSO ₄ ·2H HPAM AMPS	alkaline-surfactant-polymer calcium carbonate calcium sulfate (anhydrite) I ₂ O calcium sulfate dehydrate (gypsum) hydrolyzed polyacrylamide 2-acrylamide-2-methylpropane sulfonic acid (AMPS)	OOIP ppm PV TDS TEGBE wt%	original oil in place parts per million pore volume total dissolved solids triethylene glycol monobutyl ether percentage by weight
NVP HPLC IC IFT md NH ₃ NaCl Na ₂ CO ₃	N-vinyl pyrrolidones high performance liquid chromatography ion chromatograph interfacial tension millidarcy ammonia sodium chloride sodium carbonate	SI metric conversion factors $cp \times 1.0 E-03 = Pa s$ $ft \times 3.048 E-01 = m$ $ft^2 \times 9.290304 E-02 = m^2$ $ft^3 \times 2.831685 E-02 = m^3$ in. $\times 2.54 E+00 = cm$ $psi \times 6.894757 E+00 = kPa$	

and some sandstones. Under these circumstances, a conventional alkali such as sodium carbonate cannot be used because it precipitates as CaCO₃ as per the following reaction,

 $CaSO_4(s) + Na_2CO_3 \rightarrow CaCO_3(s) + 2Na^+ + SO_4^{2-}$

This reaction leads to consumption of alkali, retardation in pH propagation and reduction in permeability. Lopez-Salinas et al. [5], through simulations, predicted that even 0.1 wt% anhydrite can delay the pH front by 0.7 pore volumes on injection of 1 wt% Na₂CO₃. Many attempts have been made to solve this problem [6,7,8]. Sharma et al. [8] studied sodium metaborate and observed high pH propagation, good oil recovery and low surfactant retention in sandstone cores containing gypsum. They observed limited calcium precipitation on injecting sodium metaborate in a gypsum containing core by a slow reaction, but little change in permeability was observed. ShamsiJazevi et al. [7] used a sacrificial agent to reduce surfactant adsorption in gypsum containing reservoirs. Southwick et al. [9] observed ammonia to be as effective as sodium carbonate in reducing surfactant adsorption in sandstone cores. Sharma et al. [8] performed single phase alkali transport experiments with ammonia in cores containing gypsum and observed high pH propagation without calcium precipitation. However, since ammonia does not precipitate calcium ions dissolved from gypsum and gives a pH of about 11, the surfactants and polymer in the surfactant formulation must be tolerant to the calcium ions.

Significant improvements have been made in surfactant technology in recent years. Addition of ethylene oxide (EO) and propylene oxide (PO) groups have shown to increase the tolerance of anionic surfactants to divalent cations and improve surfactant phase behavior. EO/PO numbers can be tailored as per the requirement. New surfactants have been developed that are able to perform extremely well under harsh conditions such as oils with high equivalent alkane carbon number (EACN) numbers, high salinity, high hardness and high temperature [10,11,12]. Alkoxy sulfate surfactants can be stabilized at temperatures greater than 65 °C with the use of an alkali [10]. However, in the presence of gypsum, a conventional alkali such as sodium carbonate cannot be used for increasing the pH [4,13]. Ammonia may be used in such cases as it is shown to propagate a pH of 10–11 in gypsum containing cores without precipitating calcium ions.

Polymers are used to increase the viscosity of the surfactant bank and provide a separate polymer bank (behind the surfactant bank) to displace the oil bank in a stable manner. Hydrolyzed polyacrylamide (HPAM) polymers, shown in Fig. 1, are commonly used in chemical EOR. Levitt and Pope [14] have shown that HPAM polymers are stable in high salinity brines up to about 170,000 ppm NaCl. As the NaCl concentration in brine increases, HPAM solution viscosity decreases up to about 40,000 ppm, but does not change between 40,000 and 170,000 ppm. However, these polymers are shown to undergo precipitation in the presence of divalent cations depending on their degree of hydrolysis (τ). Previous studies on HPAM suggest that these polymers are susceptible to precipitation in presence of calcium ions when $\tau > 0.35$, but it also depends on the calcium concentration, temperature and salinity [14,15]. Further, HPAM hydrolysis is faster under acidic or alkaline conditions, compared to the neutral pH. Levitt and Pope [16] studied HPAM hydrolysis in detail and observed significant hydrolysis within 1–2 months in the presence of Na₂CO₃ at room temperature. They performed experiments with extensively hydrolyzed PAM and recommended using HPAM when calcium concentration is lower than 400 ppm at high salinity at 23 °C, but the critical calcium concentration is also a function of temperature.

Replacing some acrylate moieties with monomer units such as 2-acrylamide-2-methylpropane sulfonic acid (AMPS) or N-vinyl pyrrolidones (NVP) is found to increase the calcium tolerance. Levitt and Pope [14] observed a fourfold increase in calcium tolerance on using AMPS substituted PAM. The ter-polymers of NVP, AMPS and AM moieties are found to be even more tolerant to divalent ions and showed good transport properties in porous media [17,18].

In this work, ammonia was studied as an alternate alkali to perform ASP floods in presence of gypsum. Experiments were performed to study the effect of calcium ions dissolved from gypsum on various aspects of a surfactant flood, for example, surfactant phase behavior and polymer stability when ammonia was used as the alkali. Simulations were performed in a geochemical simulator, PHREEQC, to identify ways to design a robust surfactant coreflood. The results of the corefloods were compared with



Fig. 1. Chemical structure of partially hydrolyzed polyacrylamide.

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