



SPE 116214

Effect of Brine on Hydrate Anti-Agglomeration

J.D. York, SPE, Yale University, Chemical Engineering; and A. Firoozabadi, SPE, Yale University, Chemical Engineering, and Reservoir Engineering Research Institute

Copyright 2008, Society of Petroleum Engineers

This paper was prepared for presentation at the 2008 SPE Annual Technical Conference and Exhibition held in Denver, Colorado, USA, 21–24 September 2008.

This paper was selected for presentation by an SPE program committee following review of information contained in an abstract submitted by the author(s). Contents of the paper have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Electronic reproduction, distribution, or storage of any part of this paper without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to an abstract of not more than 300 words; illustrations may not be copied. The abstract must contain conspicuous acknowledgment of SPE copyright.

Abstract

Due to availability, as well as economical and environmental considerations, natural gas is projected to be the premium fuel of the 21st century. Natural gas production poses risk of flow-line hydrate blockage from co-produced water and hydrate-forming species. Common industry practice is the use of large doses of thermodynamic inhibitors such as alcohols; aside from undesirable environmental consequences, sufficient quantities of such thermodynamic inhibitors induces salt precipitation from co-produced water. Thermodynamic inhibitors affect bulk phase properties and inhibit hydrate formation. An alternative is changing interface properties by polymers and surfactants, effective at 3 to 0.5 % (or less) by weight of co-produced water. One group of low dosage hydrate inhibitors (LDHI) are kinetic inhibitors, which affect nucleation rate and growth. A second group of LDHI are anti-agglomerants, which prevent agglomeration of small hydrate crystallites. Despite great potential, work on hydrate anti-agglomeration is very limited. This work centers on the effect of NaCl and MgCl₂ in mixtures of two vastly different anti-agglomerants. We use a model oil, water, and tetrahydrofuran as a hydrate-forming species. Results show that both salts—added in sufficient quantities—may result in the agglomeration of hydrates. Our results reveal a non-monotonic agglomeration behavior at low salt and/or large surfactant concentrations. Specifically, dissolved MgCl₂ results in agglomeration more than the dissolved NaCl. Our measurements also show that the quaternary ammonium salt—*i.e.*, quat—is more sensitive to dissolved salt than the nonionic rhamnolipid biosurfactant. In this work we show that the rhamnolipid biosurfactant is effective to a low concentration of 0.05 wt. %, yet quat has effectiveness down to 0.01 wt. %. The biosurfactant—with less toxicity and higher biodegradability—is an attractive alternative to chemical surfactants in anti-agglomeration. Results on the model systems show the promise for testing in real fluid systems and the field testing of the ideas.

Introduction

Due to potential supply from various subsurface formations and clean-burning characteristics, natural gas may provide a larger share of primary energy and surpass oil consumption in the twenty-first century. There is less CO₂ produced from burning natural gas than other fossil fuels. Furthermore, produced CO₂ can be separated from the combustion products and sequestered more readily than oil combustion products for improved oil recovery or storage in saline aquifers. However, thermodynamic conditions existing in gas production lines often favor formation of crystalline inclusion compounds known as gas hydrates. Water, co-produced with natural gas, forms lattice structures by hydrogen bonding; the structures are stabilized by guest molecules such as methane, propane, *etc.*, under high pressures and temperatures in the range of a few degrees to 25 °C (Sloan, 1998). Formation of gas hydrates occurs rapidly—unlike corrosion, scale, or wax buildup. This rapidity has undesirable safety and environmental consequences. Hydrate plug formation may lead to production shutdowns and even explosions due to large amounts of methane often contained within such plugs.

Traditional hydrate prevention methods include physical means, such as insulation and electrical heating. Change of bulk phase properties through thermodynamic inhibition with methanol (MeOH) and monoethylene glycol (MEG) is widely used. Thermodynamic inhibitors shift equilibrium conditions to lower temperature and higher pressure (Dholabhai et al., 1997). Although well-characterized, these inhibitors often require large concentrations—as high as 60 weight % of co-produced water—which increase costs and have serious environmental impacts (Anderson and Prausnitz, 1986). An additional problem is that large concentrations of such inhibitors induce precipitation of salts when present in co-produced water (Masoudi et al., 2006). Such precipitation could lead to additional flow assurance problems.