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Natalia K. Kondrasheva, Viacheslav A. Rudko, Dmitriy O. Kondrashev, Renat R. Gabdulhakov, Ivan O. Derkunshtii,* and Rostislav R. Konoplin

Perspectives on Gas Hydrates Cold Flow Technology

Erlend O. Straume,[†] Rigoberto E. M. Morales,^{*†} and Amadeu K. Sum[‡][†]Multiphase Flow Research Center—NUEM, Graduate Program in Mechanical and Materials Engineering—PPGEM, Federal University of Technology of Paraná, Curitiba, Paraná, 80230-901 Brazil[‡]Hydrates Energy Innovation Laboratory, Chemical & Biological Engineering Department, Colorado School of Mines, Golden, Colorado 80401, United States

ABSTRACT: Gas hydrates cold flow can be defined as flow of non-adhesive and non-cohesive hydrate particles dispersed in the production fluids flowlines. Implementation of cold flow related hydrate management strategies might significantly reduce the costs of oil and gas field development and production by removing or reducing the need for injection of chemicals, insulation, and heating. Several research groups have performed experiments focusing on different methods of producing hydrate dispersion. Hydrate particles can be seeded into the production fluids at hydrate stable conditions to initiate controlled growth of hydrates as the dispersion is cooled to temperature conditions in production systems. Alternatively, the water droplet size in water in oil dispersions can be reduced by utilizing static mixers, high velocity, or small concentrations of chemicals, which might facilitate readily conversion of the small water droplets into hydrate particles. One researcher has proposed separating liquid phases from gas and supercooling of liquid phases before mixing the phases for hydrate formation. Use of anti-agglomerants combined with reducing viscosity by increasing water content has been proposed by other researchers. Cold flow as a component of a natural gas dehydration process is described in a patent application but has not been experimentally tested. Laboratory-scale flow loop experiments indicate that cold flow works well for low to medium gas/oil ratios and up to 20% water cut for both oil and condensate dominated systems. Experiments with crude oils containing wax show that cold flow could significantly reduce or eliminate wax deposition on pipeline walls. A field trial of the cold flow method in a once-through flowline focused on reducing droplet size, resulting in hydrate deposition. This review discusses utilized methods and published results on cold flow from various research groups in light of known mechanisms for hydrate formation. Some suggestions are also given with focus for future research in order to develop, validate, and implement cold flow as a reliable technology for hydrate management method in the production of hydrocarbon fluids.

1. INTRODUCTION

Gas hydrates have been known as a challenge for the oil and gas industry since Hammerschmidt¹ in 1934 discovered that hydrates caused blockages of pipelines. Avoiding formation of hydrates by injection of thermodynamic inhibitors such as methanol and glycols has been the traditional strategy to solve potential hydrate problems, which typically require 10–50 wt % inhibitor added to the water phase. However, this approach might not be profitable in some cases because of the large inhibitor volume.²

During the past few decades, oil companies have also started using low dosage hydrate inhibitors (LDHIs) as a means of inhibiting hydrate blockages, which might be efficient at concentrations as low as 0.01–1.5 wt %.^{3,4} LDHIs are divided into two main classes: kinetic hydrate inhibitors (KHIs) and anti-agglomerates (AAs). The mechanism for KHIs is believed to involve bonding of polymeric compounds to the hydrate surface and delaying significant crystal growth.² Recent laboratory experiments have demonstrated that certain blends of KHIs can delay measurable hydrate growth for more than 24 h at 15.9 °C subcooling.³

1.1. Promoting Flowable Hydrate Slurry by AAs. AAs are surface active chemicals that prevent agglomeration of hydrates by reducing particle adhesion. Many AA blends contain quaternary ammonium salts as active components. These ionic compounds have one or two long chain hydrocarbon tails (8–18 carbon atoms) and a hydrophilic

headgroup consisting of two or three *n*-butyl, *n*-pentyl, and isopentyl groups. However, these AAs are most efficient at water cuts below 50%.⁵ Newer studies have demonstrated that several different classes of molecules might be efficient as AAs. This includes ionic AAs of cationic surfactants such as quaternary ammonium salts, anionic surfactants such as sodium dodecyl sulfate, some non-ionic surfactants, and some normal alkanes such as normal octane and decane. Salts might also promote anti-agglomeration when combined with some AAs.^{6,7} The detailed mechanisms for interaction between different categories of AAs and hydrates are not fully understood, but it is suggested that their efficiency is determined by the absorption of the molecules on the hydrate surface, which is related to hydrogen bonding and structural fit.⁷ Theories on how AAs work are an evolving research topic, which will not be discussed in detail in this work. The discussion about AAs is limited to the particular cold flow application where use of AAs is an important component of the technology. However, for this review of the various cold flow methods proposed by different research groups, it is useful to note that there are a variety of efficient AAs available and that experiments show that AAs have a positive effect on hydrate slurry formation for water cuts from 0 to 100%.^{3,4,6,8}

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