EXPERIMENTAL AND MODELING OF METHANE HYDRATE EQUILIBRIUM CONDITIONS IN POROUS MEDIUM

Qiu-Yan Mu, Li-Tao Chen, Zheng-Wei Ma, Qin-Zhang, Chang-Yu Sun*, Bei Liu, Guang-Jin Chen*
State Key Laboratory of Heavy Oil Processing
China University of Petroleum
Beijing, 102249
CHINA

Julian Y. Zuo
DBR Technology Center
Schlumberger
9450-17 Ave, Edmonton, AB, T6N 1M9
CANADA

ABSTRACT
Phase equilibrium conditions of methane gas hydrate in SBA-15 zeolite and porous silica gels system were measured by the step-heating method. Porous medium with mean pore diameter of 5.47 nm, 6.35 nm, 10.25 nm, and 13.46 nm were adopted. The experimental data show that the equilibrium pressure will increase significantly with the decrease of pore diameter of porous medium. A thermodynamics model was developed to predict the hydrate – water – gas equilibria in porous medium based on the reaction – adsorption two - step formation mechanism by considering the effect of capillarity. The interfacial tension values between hydrate and water are determined by Gibbs- Thomson relationship. The results showed that methane hydrate phase equilibrium conditions in porous medium with different pore diameters predicted by the thermodynamics model developed in this work are superior to that of the traditional van der Waals – Platteeuw type model.

Keywords: gas hydrate, model, phase equilibria, porous medium, interfacial tension

INTRODUCTION
It was estimated that giant amount of natural gas hydrates exist in the permafrost zone and the sediments beneath the seafloor [1]. Natural gas hydrates in sediments are in general dispersed in pores of fine-grained silts, muds and clays or fractures in geological formations. It is known that the sediments inhibit hydrate formation and change the stability condition. Handa and Stupin [2] were probably the first who measured the hydrate inhibition in mesoporous medium where the inhibition was attributed to the depression of water activity. Ever since, experimental studies on the effect of narrow pores [3-13] have been reported. Uchida et al. [3] measured the dissociation of methane hydrate in three Vycor glass samples with pore diameter of 5, 15, 25 nm. They also measured the dissociation condition of methane, carbon dioxide and propane in porous glass with pore diameter of 4-100 nm [6]. Seo et al. [8, 13] measured methane and carbon dioxide hydrate phase behavior in small porous silica gels of nominal diameters 6-30 nm, and ethane and propane hydrate in porous silica gel with the pore...