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Experimental study of hydrate dissociation in oil-dominated systems using a high-pressure visual cell

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ABSTRACT

To investigate hydrate dissociation process and manage hydrate risks efficiently in oil-dominated systems, a high-pressure cell equipped with visual windows was newly constructed where hydrates were firstly formed from natural gas + diesel + water systems for a water cut of 30% and then dissociated by heating, depressurization and methanol injection. Based on the experimental data of hydrate morphologies and thermodynamic parameters, hydrate macroscopic morphological evolvement together with dissociation rate and dissociation efficiency were analyzed for each dissociation method. The experimental results indicate that hydrates dissociate faster in strong shear areas and show shrinking core character when dissociating in oil-dominated systems. Macroscopic morphological evolvements are different for the three dissociation methods, which mainly include the way hydrates fall off the cell wall, the number and rate gas bubbles form and whether ice phase would appear. Gas migration pathway is firstly observed in depressurization dissociation and a macro physical model describing pipeline hydrate depressurization dissociation is proposed accordingly. A hydrate dissociation kinetic model with a good accuracy is established by using subcooling degree as the driving force. In experiments, dissociation rate and dissociation efficiency grow with the increase of heating temperature, depressurization rate and methanol concentration. However, self-preservation effect caused by ice formation would lead to a sharp decrease in dissociation rate and dissociation efficiency in depressurization processes. On experimental conditions, depressurization has the highest average dissociation rate while heating has the lowest average dissociation rate. The average dissociation rates in experiments are between 6.40×10^{-4} ~ 2.09×10^{-1} mol min^{-1}.

1. Introduction

Natural gas hydrates (NGH) are crystalline solids composed of water and gas molecules such as methane, ethane, propane, and carbon dioxide (Sloan, 2003). NGH are easy to form when the ambient temperature is relatively low and the ambient pressure relatively high (Sloan et al., 2010). Since the first explicit hydrate plugging incident was identified in 1934 (Hammerschmidt, 1934), NGH have always been found in oil production systems (Sloan, 1998). In addition, with the development tendency of oil industry moving towards deep sea and ultra-deep sea, hazards caused by hydrate plugging are now posing a severe threat to the subsea flow assurance (Sohn et al., 2015; Li et al., 2015; Song et al., 2017). Generally, once plugs form, the remediation of them may require weeks of operating downtime and the consequent economic losses caused by production break and hydrates removing can be quite huge (Jassim et al., 2010).

In actual production processes, there are essentially four methods for hydrate dissociation and remediation, pressure method, thermal method, chemical method and mechanical method. Pressure method includes one-sided depressurization and two-sided depressurization and is most widely used in industry. However, hydrostatic head greatly limits the application of pressure method in deep sea systems (Davies et al., 2006). Thermal method aims at increasing the temperature of hydrates above the equilibrium point. Heated bundle, electrical heating (Nysveen et al., 2007), mud or fluid circulation, and external heat tracing are frequently used thermal methods. Chemical method uses thermodynamic

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Nomenclature

A,B,C,D	constants
A_s	superficial area of the hydrate particle, m^2
k	dissociation rate constant, $mol \cdot min^{-1} \cdot m^{-2} \cdot {}^\circ C^{-1}$
K	dissociation rate constant, $min^{-1} \cdot {}^\circ C^{-1}$
r_c	radius of the hydrate particle, m
r_0	initial radius of the hydrate particle, m
T	experimental temperature, °C
T_{eq}	hydrate equilibrium temperature, °C
t	dissociation time, min
v	average dissociation rate, $mol \cdot min^{-1}$
Δn	the amount of natural gas resulting from hydrate dissociation, mol
ΔP	pressure drop before and after depressurization dissociation, MPa
ΔT	the difference between heating temperature and hydrate equilibrium temperature, °C
η_D	dissociation efficiency for depressurization dissociation, $mol \cdot MPa^{-1}$
η_H	dissociation efficiency for heating dissociation, $mol \cdot min^{-1} \cdot {}^\circ C^{-1}$
η_M	dissociation efficiency for methanol injection dissociation, $mol \cdot min^{-1}$
ρ	molar density of natural gas in the hydrate particle, $mol \cdot m^{-3}$
ω	mass concentration of methanol, %

hydrate inhibitors (THIs) to avoid or dissociate hydrates (Karamoddin and Varaminian, 2014; Kim et al., 2015; Huo et al., 2001; Joshi et al., 2013; Sun et al., 2015; Kelland, 2006; Villano and Kelland, 2011; Zhao et al., 2015b). Methanol or glycol injection is a typical chemical method in offshore operations. Mechanical method mainly refers to coiled tubing, which has been used effectively where access is possible (Jaworsky and Williams, 1993; Nepomiluev and Streletskaya, 2014).

It should be noticed that, in actual production processes, methods for hydrate dissociation are used not only when hydrates have already plugged the pipeline but also used when there are only hydrates form but no plug forms in the pipeline. For example, with the help of modern detection methods, hydrate formation can be easily identified in the initial stage by the abnormality of flow parameters and other auxiliary parameters such as acoustic wave and medium conductivity before hydrate plug forms. Under this circumstance, hydrate dissociation methods are usually taken without production break in order to reduce unnecessary losses. What's more, late in the stage of hydrate plug remediation, production restart is usually attempted when most hydrates have been dissociated, which means that there is still a proper amount of hydrates in the pipeline. In these two cases, hydrate dissociation methods are used in the presence of flow motion, which this paper mainly represents.

In academic field, investigations of hydrate dissociation mainly focus on dissociation mechanisms, mathematical dissociation models and hydrate recovery in the porous medium. For dissociation above freezing point, the dissociation mechanisms can be divided into thermal mechanism and depressurization mechanism. Interfacial heat transfer controlled mechanism (Kamath et al., 1984) and moving boundary ablation mechanism (Ullerich et al., 1987) are two widely accepted thermal mechanisms. The depressurization mechanism describes an intrinsic kinetic process including lattice fracture and gas desorption (Kim et al., 1987). For dissociation below freezing point, the dissociation mechanisms mainly focus on the interpretation of self-preservation effect (Handa, 1998). According to different dissociation mechanisms, various mathematical dissociation models are proposed, such as thermal models, depressurization models, mass transfer models and synthetical models (Sun and Chen, 2006; Goel et al., 2001). Dissociation driving force and interphase heat and mass transfer resistance are the two key points in dissociation mathematical modeling. For hydrate recovery in the porous medium, researchers also have performed a great deal of work and made many achievements on it (Kamath et al., 1991; Zhao et al., 2015a; Fan et al., 2006).

However, there is still a dearth of information on hydrate dissociation in the pipeline or in oil-water emulsion (Boxall et al., 2008). Peters et al. (2006) investigated hydrate dissociation in a pipeline using two-sided depressurization method. Boxall et al. (2011) analyzed the feasibility of direct electrical heating (DEH) for pipeline hydrate plug dissociation. Unfortunately, hydrate morphological evolvements during the dissociation processes were not mentioned in the two researches above. Lachance et al. (2008) observed that hydrate particles would agglomerate in the emulsion during dissociation process when carrying out experiments using differential scanning calorimeter (DSC) and visual techniques. In experiments, this agglomeration could result in free water formation and emulsion breaking. By utilizing focused beam reflectance measurement (FBRM) and particle video microscope (PVM), Chen et al. (2014) further found that the dissociated water coating hydrate particles could account for the particle agglomeration in dissociation process. In addition, many other researches on hydrate dissociation morphology have been carried out using visual techniques such as scanning electron microscope (SEM), microscopic imaging, and X-ray computed tomography (Ju et al., 2005; Ilhan et al., 2007; Gupta et al., 2009). However, these researches analyze hydrate particle dissociation mainly in a micro scale. Consequently, much more work still needed to be done on macroscopic morphological evolvements of hydrates in the dissociation process.

In the present work, a high-pressure cell equipped with visual windows was newly constructed. Through this apparatus, hydrate dissociation experiments in natural gas + diesel + water systems were performed for a water cut of 30%. Based on the experimental results, three kinds of hydrate dissociation processes using three different dissociation methods were analyzed. Firstly, hydrate macroscopic morphological evolvements were compared between different dissociation processes. Then, a dissociation kinetic model together with a macro physical model describing pipeline hydrate depressurization dissociation were established. Finally, dissociation rate and dissociation efficiency were studied for the three dissociation methods.

2. Experimental section

2.1. High-pressure cell system

To investigate hydrate dissociation process in oil-water emulsions, a high-pressure cell, which is shown in Fig. 1, was newly designed and constructed by the Shandong Key Laboratory of Oil-Gas Storage and Transportation Safety in China University of Petroleum (East China). The main body of the cell is made of stainless steel and has a total volume of 950 ml. The design pressure of the cell is 10 MPa and the design temperature ranges from −20–100 °C. In order to observe hydrate dissociation process conveniently and directly, two circular visual windows (Φ65 mm) are installed on the front center and back center of the cell. In this work, hydrate morphological evolvements were collected by a high magnification