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# Analytical investigation of high temperature 1 kW solid oxide fuel cell system feasibility in methane hydrate recovery and deep ocean power generation

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## HIGHLIGHTS

- A dynamic Solid Oxide Fuel Cell (SOFC) model was developed.
- Hydrate bed methane dissociation model was integrated with the SOFC model.
- SOFC operated steadily for 120 days at high pressure deep ocean environment.
- Burning some of the dissociated gas for SMR heat leads to more net methane produced.
- Higher SOFC fuel utilization produces higher integrated system efficiency.

## ARTICLE INFO

## ABSTRACT

Methane hydrates are potential valuable energy resources. However, finding an efficient method for methane gas recovery from hydrate sediments is still a challenge. New challenges arise from increasing environmental protection. This is due in part to the technical difficulties involved in the efficient dissociation of methane hydrates at high pressures. In this study, a new approach is proposed to produce valuable products of: 1. *Net methane gas recovery from the methane hydrate sediment*, and 2. *Deep ocean power generation*. We have taken the first steps toward utilization of a fuel cell system in methane gas recovery from deep ocean hydrate sediments. An integrated high pressure and high temperature solid oxide fuel cell (SOFC) and steam methane reformer (SMR) system is analyzed for this application and the recoverable amount of methane from deep ocean sediments is measured. System analysis is accomplished for two major cases regarding system performance: 1. Energy for SMR is provided by the burning part of the methane gas dissociated from the hydrate sediment. 2. Energy for SMR is provided through heat exchange with fuel cell effluent gases. We found that the total production of methane gas is higher in the first case compared to the second case. The net power generated by the fuel cell system is estimated for all cases. The primary goal of this study is to evaluate the feasibility of integrated electrochemical devices to accomplish energy efficient dissociation of methane hydrate gases in deep ocean sediments. Concepts for use of electrochemical devices (e.g., high temperature fuel cells) for methane gas recovery from hydrates and efficient electricity production from the released gases are developed. The technical feasibility of these integrated systems for operation in hydrate reservoirs in deep ocean sediments was then evaluated using combined systems of thermodynamic and heat transfer equations, which are presented in detail.

## 1. Introduction

Currently, oil and natural gas are the world's primary energy resources. Methane hydrate deposits are abundant throughout the world and have been estimated to represent the greatest portion of the world's fossil energy reserves. Potential worldwide resources of methane hydrate have been estimated by different authors to be in the range $3.1 \times 10^{15}$ m³ [1] to $7.6 \times 10^{18}$ m³ [2]. Detailed examinations showed that potential resources are in the order of $1.5 \times 10^{16}$ m³ [3,4]. Based on the NETL report, the amount of natural gas in the hydrate form is estimated to be as much as $2 \times 10^{16}$ m³ [5]. Estimates of hydrate natural gas in the

North Slope of Alaska are in the order of $10^{13}$ ft$^3$, with additional 100's of trillions of cubic feet in other areas in the same region, and approximately $10^{15}$ ft$^3$ beneath the U.S. continental margin. Efficient extraction of these fuel resources could fulfill the world energy demand for many years. Despite the proved value of these hydrocarbon resources, no energy efficient technology for the recovery of these resources has yet been developed.

The main principles of hydrate plug formation and hydrate control were studied by Hammerschmidt in 1934 [6]. Methane hydrates are a crystal lattice, formed by water molecules in cages that contain methane molecules bonded to the water molecules by weak Van der Waals forces. Their properties and stability depend upon the values of equilibrium thermodynamic pressure and temperature. The basic cage of gas hydrate consists of a certain number of water and methane gas molecules (e.g. six water and one gas).

Potential environmental hazards of methane recovery from methane hydrate sediments regarding the green house gas production are well known. An immediate use of methane gas in power generating SOFC system could significantly increase the overall system efficiency by reducing the potential efficiency losses associated with the methane gas release in the distance between the methane hydrate bed and the on-shore power plant in case methane has to be delivered to the on-shore power plant. Today, most of the recovery systems that propose in-situ recovery mechanisms, have several risks associated with the methane gas release to ocean surface. In the proposed system of this study, these risks will be significantly mitigated by implementing sealed piping from the sediment to the reformer unit. In fact the authors believe that high efficiency of SOFC in power generation and immediate use of methane gas in SOFC reformer together can reduce these risks.

Several methods of hydrate prevention in technological systems have been developed up to now, and the most promising ones are: thermal stimulation, chemical injection/inhibition and depressurization. Several methods for hydrate formation prevention have been developed by Robinson and Ng [7]. Methane hydrates are not stable at sea level conditions, therefore in-situ energy efficient dissociation of gas hydrate and delivery of gas to the sea surface with the least amount of contamination are required. We have performed a system analysis in MATLAB/Simulink® to verify the feasibility of the integrated electrochemical devices (e.g., fuel cell system) and utilization in the hydrate reservoir in deep ocean sediments, using thermodynamic and heat transfer principles. Thermal stimulation and depressurization are the primary approaches included in this integrated system analysis. Proposed electrochemical devices, have high energy conversion efficiency and have the potential to improve the previous and current approaches of the methane hydrate dissociation in the field.

## 2. Methane hydrate properties

The temperature behavior of injection fluid and the heat capacity of hydrate sediments have been determined by Schoderbek [8]. Thermodynamic equations for the stability and solubility of methane hydrates have been derived by Tishchenko et al. and dissociation pressures have been calculated for various temperatures and salinities in the range of 273–293 K and 0–70 respectively [9]. The fugacity of methane gas and coefficients for the equation of state for the $CH_4$-$CO_2$-$H_2O$ system in deep ocean sediments have been computed numerically. Numerical calculations of the dissociation pressure in the temperature range of 273–293 (K) and water salinity in the range of 0–70, have been accomplished by the research group of Duan et al. [10–12]. Hydrate saturation values for the Malik 2L-38 site at the arctic Mackenzie Delta have been reported to be 35–40% and at Northern Cascadia Margin confirmed

to be 20–25% [13]. In one report by Colett et al., hydrate saturation in some cases exceeds 80% [14].

As provided in the literature, there are three main methods for gas hydrate recovery: 1. *Depressurization:* in which vertical wells are employed in the hydrate sediments. As a result of bringing the sediment pressure lower than the stable hydrate pressure, the gas hydrate dissociates. 2. *Thermal stimulation:* In this method, hydrate decomposition is induced by a thermal heat source operating at temperatures higher than the stable hydrate temperature. 3. *Chemical inhibitors:* this method involves displacement of methane hydrate equilibrium conditions beyond the hydrate stability zone through injecting a liquid inhibitor in the layer. It is well established that major parameters governing methane hydrate stability are *pressure, temperature* and *water salinity* [9]. Modeling gas hydrate dissociation requires the knowledge of thermodynamic properties of the hydrate so that one can determine the stability zone at the specific temperature and pressure. However, at equilibrium of the three phases in pure water, the dissociation pressure of gas hydrates is a function of temperature. Several experiments have been developed to express the relationships between the hydrate stability and thermodynamic parameters such as temperature and pressure and the local salinity (see, for example, Handa [15], Sloan [16]).

## 3. Thermal stimulation

The novel oxyfuel downhole steam generator (DSG) that has been developed by the PCI combustion group efficiently recovers methane gas from hydrate deposits while reducing the emissions. The proposed approach has the potential for carbon dioxide ($CO_2$) sequestration through $CO_2/CH_4$ exchange mechanism [17]. The results of this study, demonstrates that natural gas could be produced from hydrate sediment at an energy cost of approximately 15% of the heating value of methane gas. Parametrical study of methane hydrate dissociation in oceanic sediments, induced by thermal sources, has been accomplished for different values of permeability [18]. In that study, a semi-analytical model has been developed for the problem, based on the equilibrium in order to obtain further insight into the various parameters that can affect methane gas production. Permeability, porosity, and thermodynamic/transport properties of the system are among the parameters that have been thoroughly studied. Furthermore, the work proves that in contrast to previous studies of permafrost, the rate of hydrate dissociation depends upon the permeability of porous media in the case of oceanic sediments (i.e. less permeable sediment).

Velocity and the rate of hydrate dissociation are determined by Chatterjee et al. research group [19]. In that study, warm water has been used as a thermal source to stimulate hydrate dissociation. Total mass production of methane for various injection pressures and temperatures has been determined. In addition, it has been shown that despite the fact that the depressurization method has high energy efficiency regarding the net methane gas dissociation, it has a relatively low production rate compared to the warm water injection approach. Holder et al. have investigated feasibility of hydrate production from a thermodynamics point of view. This study shows that gas production is possible by thermally stimulating the hydrate rocks [20]. Upper and lower bounds of gas production and energy efficiency of the cyclic steam injection process have been determined by Bayles et al. in 1986 [21]. In one study, gas hydrate dissociation has been modeled as a moving boundary ablation process [22]. The model has been extended to thermal stimulation induced by hot water injection in the sediment [23]. Several experiments have been conducted by Ullerich et al. research group to calculate the rate of methane hydrate