Theoretical study of CO₂ storage as hydrates in produced natural gas hydrate formation

Sheraz Ahmad
China University of Petroleum, China

Abstract

CO₂ utilization as hydrates in vacated natural gas hydrate formations can be considered as viable approach to take emission control measures and preventive actions. In this analytical study, we build a dynamically coupled mass and heat transfer mathematical model which elaborates the unsteady behavior of CO₂ flowing into porous medium and converting itself into hydrates. It is targeted to unfold, at what physical and geological conditions hydrate growth rate can be increased with minimal induction time. The simulation results show that formation pressure and temperature distribution becomes stable at early stage of hydrate nucleation process and always remains stable afterwards. At higher pressure and low temperature conditions, the hydrate growth rate is rapid with minimum induction time, which makes it less time consuming to propagate the hydrates inside porous media sample. While, at lower pressure values the outcomes are other way around. The lower formation temperature facilitates hydrate nucleation process by pushing the equilibrium pressure limits to lower value. The hydrate growth rate increases by increasing injection pressure it also expands overall hydrate covered length in same induction period.

The results also show that the injection pressure conditions and hydrate growth rate affect other parameters like, CO₂ velocity, CO₂ permeability, CO₂ density, CO₂ and H₂O saturation inside porous medium. The termination and restoration of hydrate growth is also witnessed at right boundary of intermediate region which merges it in hydrate-free region a bit due to weak concentration flux between upper and low limit of CO₂ solubility concentration. hydrates of CO₂ and water can form during aquifer storage if the reservoir has regions where conditions of pressure and temperature are inside the hydrate forming conditions. Storage of CO₂ in natural gas hydrate reservoirs may offer stable long term deposition of a greenhouse gas while benefiting from methane production, without requiring heat. By exposing hydrate to a thermodynamically preferred hydrate former, CO₂, the hydrate may be maintained macroscopically in the solid state and retain the stability of the formation. One of the concerns, however, is the flow capacity in such reservoirs. This in turn depends on three factors; 1) thermodynamic destabilization of hydrate in small pores due to capillary effects, 2) the presence of liquid channels separating the hydrate from the mineral surfaces and 3) the connectivity of gas- or liquid filled pores and channels. This paper reports experimental results of CH₄-CO₂ exchange within sandstone pores and measurements of gas permeability during stages of hydrate growth in sandstone core plugs. Interactions between minerals and surrounding molecules are also discussed. The formation of methane hydrate in porous media was monitored and quantified with magnetic resonance imaging techniques (MRI). Hydrate growth pattern within the porous rock is discussed along with measurements of gas permeability at various hydrate saturations. Gas permeability was measured at steady state flow of methane through the hydrate-bearing core sample. Experiments on CO₂ injection in hydrate-bearing sediments was conducted in a similar fashion. By use of MRI and an experimental system designed for precise and stable pressure and temperature controls flow of methane and CO₂ through the sandstone core proved to be possible for hydrate saturations exceeding 60 %. A very common assumption is that formed hydrate will be stable and will block the flow in all directions in regions where hydrate is formed, and as a consequence hydrate could seal incomplete sealing of clay or shale. In some limits this could be practically true but in general hydrates formed in sediment cannot be thermodynamically stable. Even if the hydrate is inside stability region of pressure and temperature, the hydrate may be unstable with respect to the different component concentrations (and corresponding chemical potentials) in the different phases. In this work we present a first order Taylor expansion for thermodynamic properties outside of equilibrium and apply classical nucleation theory to estimate kinetic rates for hydrate formation kinetics and similar rates in cases of under saturation.

Results are applied in model studies of hydrate formation and dissociation in a model reservoir. Reservoirs of clathrate hydrates of natural gases (hydrates), found worldwide and containing huge amounts of bound natural gases (mostly methane), represent potentially vast and yet untapped energy resources. Since CO₂-containing hydrates are considerably more stable thermodynamically than methane hydrates, if we find a way to replace the original hydrate-bound hydrocarbons by the CO₂, two goals can be accomplished at the same time: safe storage of carbon dioxide in hydrate reservoirs, and in situ release of hydrocarbon gas. We have applied the techniques of Magnetic Resonance Imaging (MRI) as a tool to visualize the conversion of CH₄ hydrate within Bentheim sandstone matrix.
into the CO2 hydrate. Corresponding model systems have been simulated using the Phase Field Theory approach. Our theoretical studies indicate that the kinetic behaviour of the systems closely resembles that of CO2 transport through an aqueous solution. We have interpreted this to mean that the hydrate and the matrix mineral surfaces are separated by liquid-containing channels. These channels will serve as escape routes for released natural gas, as well as distribution channels for injected CO2.