PRF# 59217-ND9

Project Title: A better understanding of noble gas fractionation during natural gas migration in tight rock and water-saturated crust through two phase flow modelling

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Progress of Research

The research has been led by the PI in multiple directions as proposed by the PI in the proposal. The different directions are combined in one final work for the second period of the project. These directions include:

Topic	Participants	Output
Molecular dynamics simulation of gas transport (including noble gases) in tight pores of different materials.	Dr Jin Zhao (PDRA) from 15 October 2018 to 15 July 2019 in collaboration with Prof Andrew J Masters.	A paper is in progress of finalization
Multiscale modelling of single-phase gas transport in triple pore networks of micropores and mesopores.	Arash Rabbani, a PhD student whose work was aligned with the project. The work is being conducted in collaboration with Dr Dong Chen.	A paper is in progress of finalization
Thermodynamics description of gas transport properties (including noble gas components) in nano-capillaries using 2D-EoS.	Mark Seng, an MEng student whose work was aligned with the project. The work was carried out with collaboration with Dr Ali Takbiri.	Paper published in ACS Industrial and Engineering Chemistry Research (IECR), 10.1021/acs.iecr.9b02379
Two-phase flow modelling and experiments of noble gas at pore and continuum scale.	Dr Morteza Aminnaji (PDRA) from 1 August 2019.	A paper will be prepared

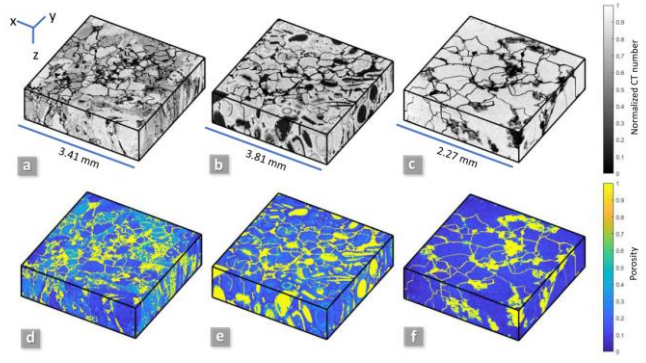
Here I briefly describe each part of the work.

1 – Molecular dynamics simulation (work in progress)

To have a deeper understanding of noble gas fractionation during natural gas migration in tight rock and water-saturated crust, classic equilibrium MD simulation method was applied to calculate the diffusion coefficients of noble gas (NG) components in the single-phase (water phase, or methane phase) and two-phase (water + methane) systems. The effects of temperature and pressure (in a range of 1 to 400 atm) on the diffusion coefficients of NG were studied to demonstrate the NG components under the reservoir conditions. Three inorganic rock materials (quartz, calcite and kaolinite) were considered to study the substrate effects on the static properties of NG. An initial configuration of water/methane/NG mixtures confined in a rectangular nano slit was established, where the nanoslit width was varied from 2 to 10 nm with different NG concentrations. Furthermore, to investigate the transport coefficients of NG, an external pressure gradient was added to the equilibrated systems to perform the follow-up non-equilibrium molecular dynamics (NEMD) simulations. **Part I:** Noble gas diffusion coefficient calculation in single phase (methane or water): to validate our simulation model, a benchmark case simulation of the noble gas diffusion coefficients in single phase (methane or water) was conducted. Periodical boundary conditions were applied to the simulation box. The diffusion coefficients of noble gas components (He, Ne, Ar, Kr and Xe) in the pure water phase, or in the pure methane phase, were calculated. Both the effects of temperature and pressure on the NG diffusion coefficients were investigated. The results show a good agreement with previous studies which indicate that the simulation setup is validated. **Part II:** Substrate effects on the diffusion coefficients. Three inorganic rock materials (quartz, calcite and kaolinite) were considered to study the substrate effects on the static properties of noble gas. An initial configuration of water/methane/NG mixtures confined in a rectangular nano pore with a length of 20 nm was established, where the nanoslit width was varied from 2 to 10 nm with different NG concentrations. Moreover, the model was further extended to add bulk-phase-like methane/water liquid in both left and right sides to demonstrate the mesopore effects around.

2 – Multiscale modelling of gas transport (work in progress)

In this part of research we extracted a triple pore network model (PNM) from micro-tomography images of heterogeneous shale/carbonate rocks and simulated steady-state gas flow through them to investigate the viability/applicability of the proposed method. We extracted PNM's consisted of meso-pores and micro-pores which were unresolved in the images. The term micro-pores were used when pores were too small to be explicitly visible in the tomography images and we could only capture shadow cast of them. On the other hand, meso-pores were clearly visible in the images and pore boundaries could be distinct from



the solid or partially solid background. After extracting the regular PNM, we included fractures and micro-porosities and finally we clarified the equations that can be used to simulate the steady-state liquid and gas flow through the PNM by considering no surface reaction or physical adsorption. The methodology will be used for better prediction of gas flow in shale rock.

Figure 1 - Fractured realizations of porous samples and corresponded porosity map of each sample, (a) normalized CT number of Estaillades carbonate rock, (b) normalized CT number of Savonnieres carbonate rock, (c) normalized CT number of Massangis carbonate rock, (d) porosity fraction map of Estaillades, (e) porosity map of Savonnieres, and (f) porosity map of Massangis.

3 –Thermodynamics description of gas transport in nano-capillaries, using 2D-EoS (work completed)

In the orders of nanometres, diffusion and adsorption effects deviate significantly from current conventional models which result in limited estimation accuracy of hydrocarbons capacity and recovery potential. At such small pore sizes, limited pore space as well as wall superimposition effects affect both adsorption and diffusion behaviour. Classical laboratory experiments carried out on nanoporous material are unable to characterise adsorption behaviour accurately due to the presence of larger macropores within the network. At present, grand-canonical Monte Carlo (GCMC) molecular simulations are usually employed to model both diffusion and adsorption effects independently. However, GCMC is computationally expensive and does not provide a quantitative variation trend of adsorption isotherm with pore size.

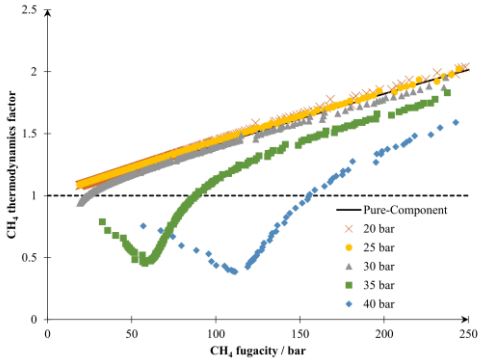


Figure 2- CH_4 thermodynamic factor at varying CH_4 pressures and constant but different CO_2 partial pressures (details in IECR paper, 10.1021/acs.iecr.9b02379).

In the paper published in IECR, a thermodynamics-based Two-Dimensional Equation of State (2-D EoS) model was introduced to characterise adsorption isotherms in small carbon and mineral capillaries. The effects of pore sizes on adsorption isotherm parameters were compared with that determined from a bulk scale predictive model. Regressed parameters from pure component isotherms were applied to a methane-carbon dioxide binary system. Results were consistent with that determined from molecular simulations. Therefore, it was concluded that by applying appropriate cubic equation of state, the 2-D EoS Adsorption Isotherm Model is able to produce an accurate quantitative representation of the adsorption behaviour in nanopores.

4 – Two-phase flow modelling and experiments of noble gas components (upcoming work)

Based on input from laboratory tests, we will combine species fractionation during transport with the adsorption/desorption rate of competitive isotopologue adsorptives expressed in the classical Langmuir equation. The novel formulation is in dual permeability format and is developed for both matrix and fracture media with transfer terms. We will use a combination of experimental methods, spanning from basic and advanced rock characterisation to petrophysical methods involving gas adsorption/desorption and permeability tests as well as mechanical tests (using X-ray CT and synchrotron imaging). In order to understand isotopic fractionation during mass transfer from matrix to fracture (by fracturing as well as by reservoir pressure reduction) and to predict fracturing intensity and reserves, we will (i) perform rock characterisation through X-ray powder diffraction (XRD), (ii) perform gas adsorption experiments to determine methane and noble gas isotope fractionation during desorption, and (iii) use medical CT, µCT, synchrotron based in-situ fracturing of shale samples leading to the production of noble gases.

Impact of the research

- The PI (Masoud Babaei): I have been extremely benefitted from the project to expand my research in directions that are completely new to me such as molecular dynamics simulation and shale gas modelling. The knowledge developed can be expanded to other areas of subsurface systems such as Enhanced Geothermal Systems (EGS) and aquifer remediation (studies at molecular scale). Based in the research track record developed from this project, I will apply for larger grants in future.
- The first PDRA (Jin Zhao): Career development as a PDRA at The University of Manchester, providing the much-needed previous employment status for applying successfully for permanent position at Beihang University.
- The second PDRA (Morteza Aminnaji): Career development as a PDRA at The University of Manchester.
- The undergraduate students (Mark Seng and Arash Rabbani): One paper is or will be published by each of undergraduate students, strengthening their CV for future applications of academic positions.
- The collaborators: I have been able to meet Dr Dong Chen at CUP-B to discuss our developments in the project. A visit of Dr Chen to The University of Manchester will occur in October 2019. Several companies in China have been approached to consider possible application of noble gas environmental tracing in their shale gas recovery projects. Several ideas of research have been initiated while discussing with Prof Andrew Masters and Dr Ali Takbiri. Finally a visit of Dr Farzam Javadpour (University of Texas at Austin) to The University of Manchester will take place in the second period of the project.