Description of the master's thesis

A significant amount of natural gas is stored in geological formations. This amount is not only trapped in conventional reservoirs, but also in unconventional ones. In the last century, traditional techniques have been used for production of natural gas from conventional reservoirs. Thus, the conventional reservoirs have become depleted over time, and the gas placed in unconventional reservoirs became more important. However, due to the low to ultra-low permeabilities of these reservoirs, application of traditional techniques for gas production from these reservoirs is not adequate.

Shale as an abundant unconventional reservoir has drawn a lot of attention during the last two decades. Considerable amounts of natural gas are stored in its matrix, but for a long period of time, the question was whether this amount could be extracted by new techniques or not. Finally in 2011, the gas production from Bernett shale in the U.S., which supplied 7% of the natural gas production of the whole continent, answered this question. This event can be considered as a milestone in shale gas history. In that year, more than twenty percent of the U.S. dry gas production was from shales [1].

The production of natural shale gas requires knowledge about the state of the gas in the shale matrix and knowledge of the production mechanism. Studies on the stored gas in shales revealed that a considerable portion is in the adsorbed state [2]. Therefore, investigations on the adsorption behavior of natural gas components can help to better estimate the amount of gas in shales (gas in place), i.e. the possible production rate. The stored amount of ethane is small in comparison to methane; however, the produced amount can be used in several industrial processes.

In this thesis, the excess sorption capacities of Black shale from Belgium for methane and ethane was investigated. We have applied the manometric method to measure methane and ethane sorption on shale at three different temperatures. Our interest was largely focused on shale occurring in the Belgian area, with an obvious application in North-Western Europe. The dry black shale of Belgium was taken from a depth of 745 m with more than 57% clay minerals and 6.58% organic matter. We investigated the results using a high-pressure manometric set-up on a dried shale sample, which has been proven to give reliable data. The manometric set-up determines the excess sorption isotherms. In essence, the experiment consist of two cells: a pressurized reference cell, which is connected to a sample cell. In order to remove all the moisture content, the sample cell has been dried in an oven for 24 hours at 378 K under vacuum conditions. The governing principle in this method is the mass balance. For calculating the void volume excluding the sample volume we introduce an inert gas to the system. As we assume the adsorption of inert gas into the sample is negligible, we can find the void volume of the sample. So, a ratio between the void volume and the reference cell can be defined, which will be used in further calculations instead of the porosity of the sample [2].

Furthermore, the difference between the total amount and the amount of free gas after equilibrium is the sorbed amount. The density used in the calculation can be obtained from the equation of state for the gas using its temperature and pressure.

The full flow scheme of the manometric set-up consists of a sample cell A and a reference cell B. The reference cell B consists of tubing with a total volume of $3.524 \times 10^{-6}$ m$^3$. The volume of the
reference cell can be enlarged to 12.152x10^{-6} m^3 by opening valve 1 to include vessel C. Two similar sample cells are used to minimize the downtime for a sample exchange; the second sample cell can be prepared while the experiment with the first sample cell is running. The volumes of these two sample cells are 78.33x10^{-6} and 75.90x10^{-6} m^3 [2].

One experiment comprises the following four sequential procedures: (a) Helium leakage test, (b) a void volume measurement by a Helium sorption experiment, (c) an actual sorption experiment with methane, and (d) a control measurement of the Helium sorption. The second Helium sorption experiment is carried out to ensure that the volume accessible to gas has not changed during the experiment. The Helium leak rate is determined at 18 MPa and at the experimental temperature for more than 24 h [2].

Figure 1: Schematic drawing of setup (left), front view of the setup in TuDelft (right)

We use an evacuation pump for the initial preparation by evacuating for 24 hours. Subsequently we fill the reference cell by opening the valve between the pump and the reference cell to a pressure $P_f$ with the valve between the sample cell and the reference cell closed. Then we open the second valve and measure the equilibrium pressure. It is not possible, however, to obtain a "true" equilibrium pressure with methane within reasonable time. Then we again closed valve "4" and filled the reference to a filling pressure as close as possible to $P_f$.

In case of methane, experiments in three different temperatures of 308 K, 318 K and 336 K and pressures up to 11 MPa are performed. A Monte Carlo simulation for error analysis of the experiment and for the possible error of the equation of state has been used. The results show that the maximum methane sorption capacity of the shale is found to be 0.013-0.039 mmole per gram of sample, which tends to decrease at increasing temperature. Excess sorption experiments on ethane are performed at a temperature of 318 K and pressures up to 9 MPa. The maximum excess sorption capacity of the shale for ethane is found to be 0.7 mmole per gram of the sample, which is more than one order of magnitude higher than that of methane.

References
