The mechanism of methane adsorption on clay minerals under geological condition

Methane present on the Earth occurs commonly in geological formations under high pressure. In the presence of water, at high pressure and low temperature, methane occurs as methane hydrates (clathrates) that are crystals, where methane molecules are trapped in the water lattice. Clathrates are present within pores in the marine sediments even up to 2000 m below the seabed. Methane also occurs in fine-grained sedimentary rocks, especially in shales and tight-sands formations, that form economically important unconventional natural gas reservoirs. The compound that links all the environments listed above are clay minerals – the most abundant mineral type in Earth's upper crust. Very high pressure cause methane adsorption on available surface, and in micropores. Adsorption phenomenon results in significant enhancement of adsorbed gas density in comparison to free gas in the same pressure. Clay minerals can contribute significantly to total adsorption capacity in listed above environments due to high specific surface area and microporosity (because of fine-grained texture and layer structure). Unfortunately, the factors that control the high pressure methane adsorption on clays have not been determined.

Clay minerals differ not only in the crystal structure, but also texturally (i.e. grain sizes). The part of clay minerals group has accessible interlayer space between each layer. Inside the interlayer exchangeable cations are located together with water molecules. As a result of drying, interlayer width could be decreased due to water removal, up to the total closing (collapse). By using different species of exchangeable cations it is possible to simulate the other clay minerals types, which have not naturally accessible interlayer space, and cations are no exchangeable.

The main aim of the proposed project is to determine the structural and textural controls (i.e. crystallites orientation) on methane adsorption on clays under high pressure, by separating the structural and textural effects that are not related to the mineral structure. Interlayer availability conditions will be investigated and the effects of methane adsorption in the interlayer will be measured.

Three types of expendable clay minerals (with modifiable interlayer width) was selected as starting materials for the research: montmorillonite, beidellite, and vermiculite. The minerals differ in the amount of exchangeable cations in interlayer space, strength of repulsive force between layers, and strength of attracting force between layers and interlayer cations.

Analysis will be done on a set of cation-exchanged (for different cation species) samples. After each step of measurements, samples will be dried in higher temperature. A result of the drying protocol will be stepwise closing of interlayer space. The interlayer-closing effect will be connected to the type of cation in the interlayer. Samples will be a subject of methane adsorption and desorption experiments in changing gas pressure, at constant temperature. Texture of the samples will be modified by using different preparation techniques (i.e. random crystallites orientation by drying of sprayed sample). Calculations of specific surface area and volume of micropores will be enabled by low-pressure adsorption analysis of CO_2 and N_2 vapors. The most promising samples will be a subject of XRD (X-ray diffraction) measurements in changing pressure of methane (in high-pressure range). This measurements will be carried out in high-pressure designed measuring chamber. This will enable observations of interlayer width change in changing methane pressure. To check the orientation and measure the size of crystallites, set of samples will be photographed, using transmission electron microscopy technique (TEM). Obtained results will be used for determination of the dependences between methane adsorption, structure, and texture of clays. It will also allow to answer the question: is the interlayer space accessible for methane and if yes in what conditions? The proposed project has a potential impact on the many scientific fields, i.e. of organic and gas geochemistry, unconventional resources evaluation, and computer modeling of adsorption.