A thermodynamic understanding of clay-swelling inhibition of interlayer potassium ion

XIANDONG LIU AND XIANCAI LU*

Department of Earth Sciences, Nanjing University and State Key Laboratory of Mineral Deposit Research. Hankou Road 22, Nanjing 210093, P. R. China;
xcljun@nju.edu.cn

The unique swelling property of smectites attracts numerous studies due to the direct application interest in many fields including oilfield and civil engineering. One remaining open issue is the swelling inhibition property of pottassium ion[1]. It is found that potassium saturated clays do not expand to osmotic steps even in aqueous suspensions. So, the potassium ion can be used as a swelling inhibitor in drilling mud to prevent the wellbore collapse typically caused by macroscopic swelling of Na-smectites. Although some studies contribute to this issue, the underlying molecular mechanism is still poorly understood. In addition, the striking stability of 1-layer K-hydrate cannot be explained. We employ molecular dynamic simulations[2-3] to study the clay-swelling inhibiting function of potassium by making detailed comparison with the contrasting case of sodium. The relative stabilities of different hydrate states are indicated by using the swelling energy curve. We find that 1-layer K-smectite hydrate is actually the global minimum of the swelling energy curve corresponding to the most stable state. It is also evident that the expansion to osmotic step is energetically inhibited. Contrastingly, the 2-layer state of Na-smectite corresponds to the global minimum of the energy curve and the osmotic swelling is preferred potentially. We study the interlay structure and dynamic behavior in 1-layer K hydrate in detail. For the first time, we find that potassium ions are all trapped and immobile in coordination cages composed of the hexagonal oxygen and water oxygen. This novel microstructure provides a microscopic interpretation to the surprising stability.

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