

Simulation of the stability of Na-, K-, and Ca-montmorillonite at high temperatures and pressures

L. DE PABLO-GALAN¹ AND M.L. CHAVEZ-GARCIA²

¹Instituto de Geología, Universidad Nacional A. de México, 04510 México, D.F., México

²Facultad de Química, Universidad Nacional A. de México, 04510 México, D.F., México

Monte Carlo grand canonical molecular simulations on the hydration of Na-, K-, and Ca-montmorillonite have shown that between 333 – 533 K and 300 – 1300 bar, Na-montmorillonite forms stable one-layer hydrates of d_{001} spacing extending from 12.64 Å to 12.38 Å. In the same range, the one-layer hydrate K-montmorillonite varies between 12.78 Å and 12.59 Å whereas that of Ca-montmorillonite changes from 12.48 Å to 12.32 Å. A two-layer hydrate of d_{001} 14.80 Å is formed by Na-montmorillonite at 533 K and 1300 bar, of 15.32 Å by K-montmorillonite under the same conditions, and of 14.74 Å stable to 533 K and 2000 bar. Ca-montmorillonite develops a 13.83 Å two-layer hydrate at 473 K and 1000 bar (1).

Correlations between the pressure tensor P_{zz} and the d_{001} spacing point that the one-layer hydrates are unstable under all conditions to high depths, whereas the two- and three-layer hydrates appear to be stable only under more limited PT environments. In the clay interlayer, Na^+ and Ca^{2+} are fully solvated within the water layers away from the siloxane surfaces, whereas the K^+ are largely on the interlayer midplane within a constricted water layer but some are closer to the clay surfaces. The $g(r)$ indicates cation – oxygen separations of 2.84, 2.60, and 2.80 Å for Na^+ , K^+ , and Ca^{2+} for the force field considered.

References

[1] de Pablo, L., Chávez, M.L., de Pablo, J.J. (2005) *Langmuir* **21**, 10874-10884..