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# Modelling specific adsorption of divalent metals on montmorillonite surfaces. Pitfalls, recent achievements and current challenges.

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In the framework of clay barrier concept for underground nuclear waste storage, montmorillonite and bentonite have been widely used as reference materials for sorption. Recently, accompanying modelling work aims at understanding and predicting sorption in more complex systems where clay are assumed to be representative of the most reactive natural phases. This “bottom-up” approach relies on a good confidence in the mechanistic understanding of sorption phenomena. The present study aims at reviewing clay sorption experimental and modelling works with a focus on divalent metals surface complexation mechanisms. Clay sorption processes together with current modelling concepts will be discussed. Based on this current knowledge, criteria will be set up to select data that are relevant for surface complexation model calibration (especially ionic strength, pH, clay preparation, metal to clay ratio and solubility limits). We identified missing information, which is necessary to model sorption data in a mechanistic way, together with experimental features that cast doubt on the ability of surface complexation models to catch adequately the nature of divalent metal sorption on montmorillonite edge surface. Problematic experimental features will be highlighted, especially those related to the reversibility of sorption (surface complexation model approaches make the hypothesis of total reversibility) and the effect of solid to liquid ratio ( $R_{SL}$ ) on sorption distribution coefficients (thermodynamic equilibrium condition agrees only with a constant distribution coefficient as a function of  $R_{SL}$ ). Neglecting these possible problems, models available in the literature will be then tested in terms of efficiency (data fit) and mechanistic likelihood.

Although the link between edge surface charge and edge surface potential is complicated by the spill-over of electrostatic field present on basal and interlayer surfaces on edge surfaces, we will show that specific sorption data at medium metal to clay ratio ( $\sim 0.01-0.05$  mol/kg<sub>clay</sub>), corresponding to sorption on low energy sites, could be modelled with a state-of-the art surface complexation model, taking into account the electrostatic potential influence on sorption intensity. However, specific sorption data at low metal clay ratio ( $< 0.001$  mol/kg<sub>clay</sub>), corresponding to high energy sites, could be modelled satisfactorily with non-electrostatic models only. The reasons for the failure of electrostatic models will be explained through the mathematical derivations of surface complexation models equations. This approach enables showing that there is no hope to reconcile high energy site sorption behaviour with a classical surface complexation electrostatic model description. Amongst other explanations, an alternative surface substitution model will be proposed that is in agreement with the current knowledge on high energy sites structural properties. According to this approach, sorption on high energy sites might be the result of a structural substitution in the edge structure instead of a surface complexation mechanism. Another explanation could be linked to the dissolution of clay upon pH increase and changes in high energy surface sites abundance. Clearly, further experimental investigations are needed to understand the nature of sorption mechanism on high energy sites.

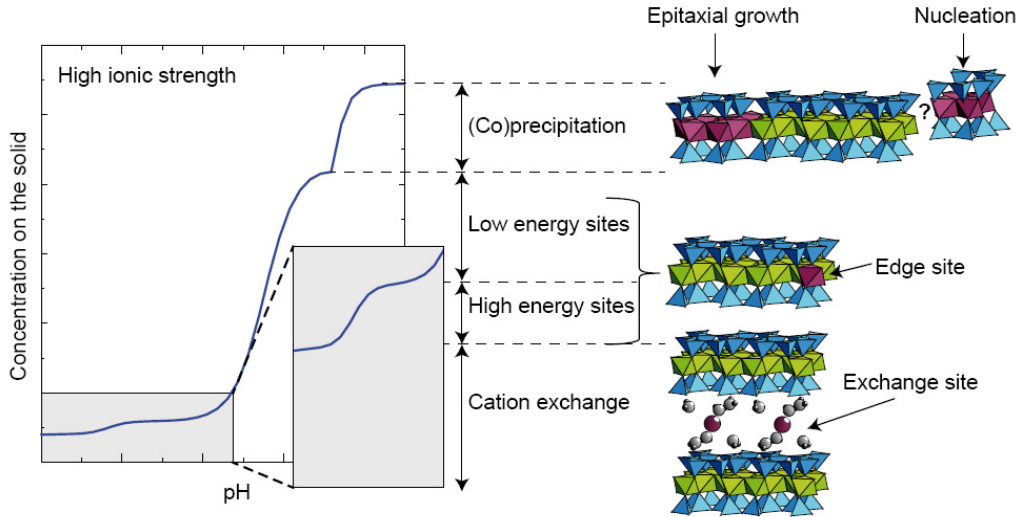


Figure 1. Relative importance of identified sorption processes as a function of pH (Schematic view). Decreasing ionic strength results in a higher contribution of cation exchange processes on the overall retention.

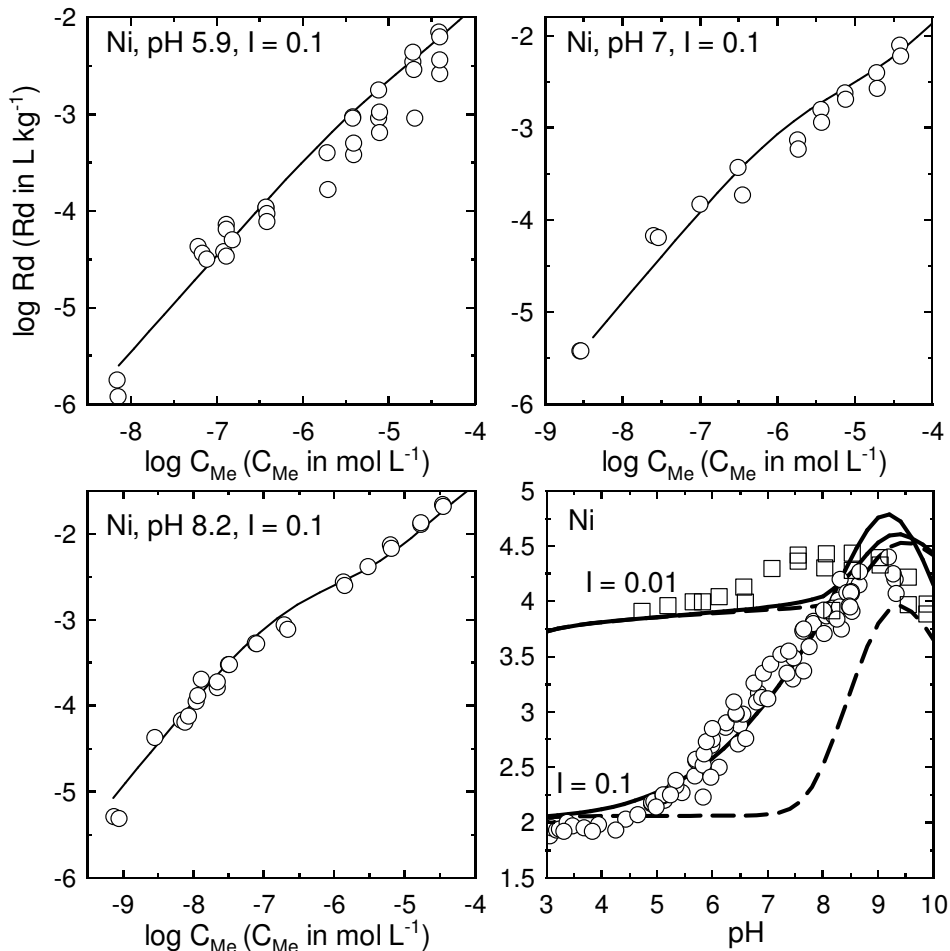


Figure 2. Electrostatic model for high energy site (substitution model) and low energy site (surface complexation). Full lines: model predictions. For Ni sorption edge, dashed lines indicate a model without strong sites contribution. Symbols: data from Baeyens and Bradbury, 1997 (A mechanistic description of Ni and Zn sorption on Na-montmorillonite. Part I: Titration and sorption measurements. *J. Contam. Hydrol.* 27, 199-222).