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# EXTENDING THE PREDICTION OF THE THERMODYNAMIC PROPERTIES OF CLAY MINERALS TO THE TRAPPING OF TRACE ELEMENTS

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## Introduction

The thermodynamic properties of clay minerals, which control the stability of these minerals in solution, are still a matter of debate in spite of recent advances (Gailhanou et al., submitted). This is especially the case for the minerals that may structurally include trace elements and potential radionuclides such like Ni, Cd, Co, Cr, Mn, Pb, ... The usual methods developed in order to predict thermodynamic properties are parameterised using a given set of minerals. For clay minerals, the latter are mainly composed by Si, Al, Fe and Mg, apart from the alkalis elements (Chermak and Rimstidt, 1989), which means that predictions are limited to minerals whose layers are composed by Si, Al, Fe and Mg. At the vicinity of H&ILW disposal cells, the possible interactions between clay rock or engineered barrier and waste degradation products can result in the appearance of clay minerals that may structurally include radionuclides within an irreversible trapping process. This work aims at proposing a method for predicting the thermodynamic properties of such minerals.

## Theoretical principle and selection of calibration phases

Vieillard (1994) has developed a methodology of estimation based on the difference of electronegativity by considering three scales of values of the parameter  $\Delta_{\text{H}}\text{O}^{\ominus}(\text{M}^{\text{z}+}_{\text{clay}})$  in the three sites of phyllosilicates. We have considered the work of Vieillard (1994) that originally applies to the estimate of  $\Delta\text{H}^{\ominus}_{\text{f}}$  and extended it to the estimate of  $C_p(\text{T})$ ,  $S^{\ominus}$  and  $V$ . Some popular estimate methods (Chermak and Rimstidt, 1989) are based on the hypothesis that the thermodynamic property of a mineral can be obtained by combining the properties of its components. An improvement of this principle had consisted in decomposing minerals into their polyhedral components (Chermak and Rimstidt, 1989). Now, we can write the fictive solution equilibrium with a basic polyhedral component  $\text{M}_x\text{O}_y$  as:  $x\text{M}^{\text{z}+}_{\text{aq}} + y\text{O}^{\ominus} = \text{M}_x\text{O}_y$  and assuming the entropy of this fictive reaction is zero, we can define a  $\Delta_{\text{S}}\text{O}^{\ominus}$  parameter as:

$$\Delta_{\text{S}}\text{O}^{\ominus}(\text{M}^{\text{z}+}_{\text{clay}}) = S^{\ominus}(\text{O}^{\ominus}) = \frac{S^{\ominus}(\text{M}_x\text{O}_y) - x \cdot S^{\ominus}(\text{M}^{\text{z}+}_{\text{aq}})}{y}$$

The value for the oxide analog of the polyhedral unit is obtained by implementing  $S^{\ominus}$  of the oxide in the  $S^{\ominus}(\text{M}_x\text{O}_y)$  term. We have also defined, from the same reasoning, similar parameters for heat capacity and volume of the basic polyhedral components:

$$\Delta_{\text{C}_p}\text{O}^{\ominus}(\text{M}^{\text{z}+}_{\text{clay}}) = \frac{C_p(\text{M}_x\text{O}_y) - x \cdot C_p(\text{M}^{\text{z}+}_{\text{aq}})}{y}; \Delta_{\text{V},\text{C}_p}\text{O}^{\ominus}(\text{M}^{\text{z}+}_{\text{clay}}) = \frac{V(\text{M}_x\text{O}_y) - x \cdot C_p(\text{M}^{\text{z}+}_{\text{aq}})}{y}$$

## Results and discussion

On Figure 1, we have displayed, for entropy, the correlation obtained between calculated values of  $\Delta_s O^-$  for the polyhedral unit and for the oxide analog. A straight line and a second-order function are obtained, for the interlayer and octahedral cations, respectively, with a good correlation coefficient.

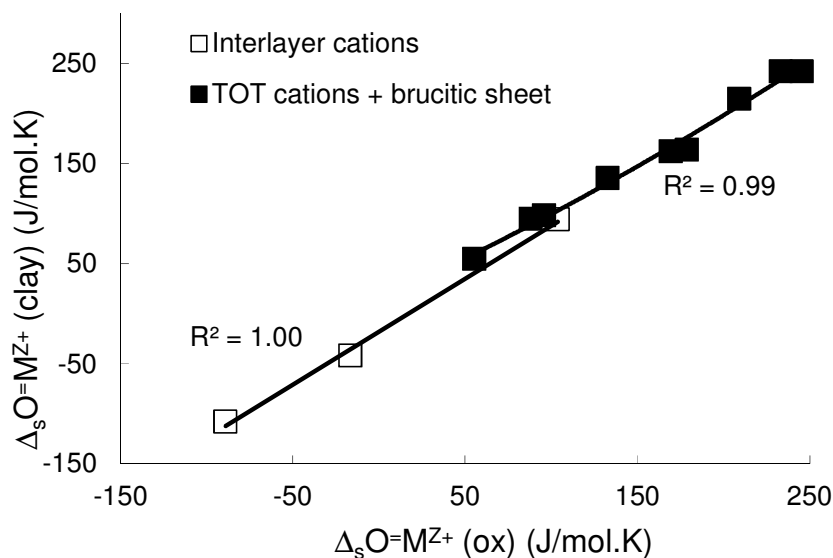


Fig. 1 - Development of predictive capacity for entropy estimates

The implementation of the derived semi-empirical, first or second order relations allows to estimate the thermodynamic properties of a clay mineral, MX80 ( $Na_{0.409}K_{0.024}Ca_{0.009}(Si_{3.738}Al_{0.262})(Al_{1.598}Mg_{0.214}Fe^{3+}_{0.173}Fe^{2+}_{0.035})O_{10}(OH)_2$ ) in the present case, loaded by 6 radionuclides and to compare the values with the results obtained by Gailhanou et al. (submitted). The results can be expressed in terms of the concentrations for the elements Ni, Cd, Co, Cr, Mn and Pb and in terms of energetic potential with respect to the measurements performed by Gailhanou et al. (submitted).

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