MODELLING TITRATION CURVES OF MIXED MATERIALS WITH VARIABLE AND PERMANENT SURFACE CHARGE: APPLICATION TO MIXTURES OF AN IRON OXIDE AND MONTMORILLONITE.

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Two well-known materials, lepidocrocite (specific surface area 116 m²g⁻¹) and montmorillonite (internal surface area 700 m²g⁻¹), can be useful to test the mathematical model described in the preceding communication. With this purpose, acid and base titration curves of both minerals and of mixtures containing 80% (w/w) of lepidocrocite (sample LM) and 80% montmorillonite (sample ML) were obtained at three ionic strengths (0.01, 0.1 and 1 M NaCl). The amounts of titrant consumed by the suspensions at each pH were corrected for the amount consumed by the corresponding solution at the same pH. The resulting graphs are shown in next page. Dashed lines will be explained later.

It is readily evident that the curves corresponding to pure lepidocrocite and LM are very similar to those observed in the literature for oxides and many variable charge soils, with a crossover point (point of zero salt effect, PZSE) approximately corresponding to the zero point of titration. Sposito (1984) concluded that the point of zero net charge (PZNC) and the PZSE are equal for solids with no specific affinity for the electrolyte ions, so that in the PZSE $\sigma_{ox} + \sigma_{cl} (\sigma_H$ of Sposito, 1984) equals $-\sigma_p$ as long as $\sigma_0 < 0$. A study of a wide variety of outputs of the model (Madrid and Diaz-Barrientos, in press) showed that when a crossover point was apparent in $\sigma_{ox} + \sigma_{cl}$ vs. pH plots it happened at $\sigma_{ox} + \sigma_{cl} = -\sigma_p$, in agreement with the conclusion of Sposito (1984). This result provides a tool to con-
vert experimental ordinates to an absolute scale of $\sigma_{ox} + \sigma_{cl}$ when a crossover point is present. This is the case of the curves for lepidocrocite, $R=0$, and sample LM, $R=0.6$ (60% of the surface area of the mixture is calculated to correspond to montmorillonite). When $R \neq 0$, the correction term, $-\sigma_p R$, must be included in the optimization routine of the computer program if $\sigma_p$ is one of the adjustable parameters. When $R=0$ the correction is obviously unnecessary.

For montmorillonite and ML, the crossover point no longer appears within the pH range studied, but there is an inflexion point near the initial point of titration, where the curves obtained at different ionic strengths run very close to one another. A similar point of inflexion appears in outputs of the model when $R$ is close to 1 (data to be published) and its ordinate is always $\pm N_{ox}(1-R)$. The reason for this behaviour of the model is not clear, but can be used to convert the p.d.i. adsorption axis to $\sigma_{ox} + \sigma_{cl}$ when no crossover is apparent. For a pure clay, the $\sigma_{ox} + \sigma_{cl}$ values must be the same as those for p.d.i. adsorption, as
In the case of ML (R=0.95) the correction was also included in the program, as $N_{ox}$ is one of the adjustable parameters.

The dashed lines show the results of the best fit of the model for each material (they are visible only in those regions where they can be distinguished from the experimental curves at the scale of the drawing). Pure lepidocrocite gave the values $N_{ox}=3 \times 10^{-9}$ eq.cm$^{-2}$, $G_{ox}=9 \times 10^{-13}$ eq.cm$^{-2}$.mV$^{-1}$, $G_{d}=1$, $K_{Hox}=1.2 \times 10^8$, $K_{0Hox}=2.6 \times 10^6$, $K_+=0.09$, $K_-=0.01$, and montmorillonite $N_{cl}=3.5 \times 10^{-11}$, $K_{HCl}=2.0 \times 10^3$, $K_{0HCl}=8.0 \times 10^3$, $G_{cl}=10^{-8}$, $\sigma_p=2.5 \times 10^{-11}$. The significance was high ($P<0.01$) in both cases.

The best fit for LM and ML gave very similar values of most parameters except $N_{ox}$, which resulted considerably smaller in both mixtures ($1.9 \times 10^{-10}$ for LM and $8.2 \times 10^{-11}$ for ML). This unexpected result could suggest that the clay, with a much higher surface area than the oxide, interacts with the latter in such a way that it is able to block in a considerable degree the access of the adsorbing ions to the oxide. This assumption is supported by the fact that the value of $N_{ox}$ is smaller the higher the value of R. More information is necessary to confirm this hypothesis, so that it should be taken carefully.

REFERENCES