Water-cation interaction in Na or Ca saturated montmorillonite interpreted by neutron scattering

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Water retention controls smectite swelling which underpins the ability of clays to act as barriers round hazardous waste sites. As the relative humidity changes so does the volume of the clay hence controlling and defining the clay-water interaction is of considerable industrial interest. Water in clay can be broadly separated into three categories: (a) interparticle (or external) water which exists outside and between quasi-crystals, (b) water in the clay interlayer as the cation hydration shell and (c) interlayer water outside the cation shell. In this project we aimed to compare water in the three states in montmorillonite with halloysite which has no cations present in the interlayer. For this Conference we describe recent data (June 2010) defining the water present in Na and Ca saturated SAz-1.

Quasi-Elastic Neutron Scattering (QENS) from clay is dominated by the neutron scattering from hydrogen atoms and to a first approximation all other scattering can be ignored. In fact when careful corrections are made to QENS data to remove the non-hydrogen scattering the spectra can be used to quantitatively differentiate between the different hydrogen motions in clays. When QENS spectra are compared to the resolution function of the instrument it is possible to distinguish between the elastic scattering, which nominally defines the structurally bound water (within the window defined by that resolution function) and the quasi-elastic scattering which defines the motion of water in the three categories described above.

In earlier work (Bordallo et al., 2008) we compared QENS data for charge-reduced sodium saturated Jelšovỳ Potok montmorillonite with Te Puke Halloysite at P/Po =0.54 before and after heating to 300°C to remove water. The heated montmorillonite was in a charge-reduced form hence it was possible to differentiate between the interlayer water and interparticle water. In the same work a fixed elastic window technique was used to compare the amount of elastic scattering of the two clays as a function of temperature, enabling us to separate the different motions of the water in the clay. At 10K all motion is quenched hence all neutron scattering is elastic and the intensity of the elastic scattering peak can be set to unity. As the clay is warmed up water moves by vibration and the elastic peak reduces. Plotting the reduction of intensity against temperature, at the three instrumental resolutions used 1, 25 and 100 μeV, enables identification of when motion begins. Different types of motion such as rotation or translation will begin at different temperatures. It was estimated that about 23% and 47% of the hydrogen in the smectite and the halloysite were bound as hydroxyl groups, which

compares well with chemical analysis. At 1 μeV resolution it can be inferred that almost all of the water was mobile as the intensity variation appears to become approach a constant value at room temperature fractions.

Figures 1 and 2 illustrate the onset of vibrational, rotational and translational mobility at the different temperatures and at the different instrument resolution. It is important to realize that different resolutions give insight to different time windows. Using methods outlined in Lechner (2001) the time window at which the different motions can be distinguished and this is illustrated in Table 1.
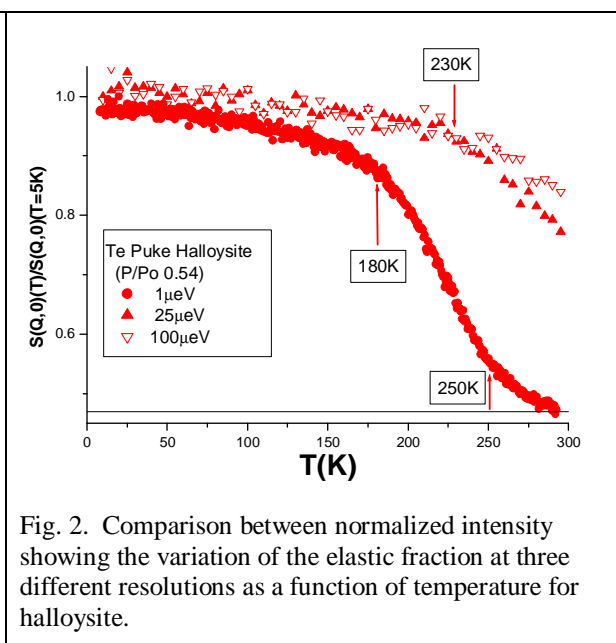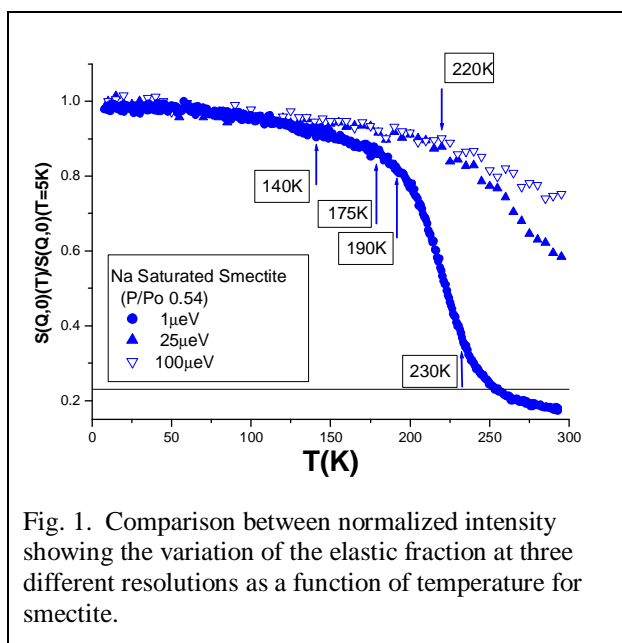

Fig. 1. Comparison between normalized intensity showing the variation of the elastic fraction at three different resolutions as a function of temperature for smectite.

Fig. 2. Comparison between normalized intensity showing the variation of the elastic fraction at three different resolutions as a function of temperature for halloysite.

Table 1. Time windows where water motion is distinguishable from QENS ToF spectra.

Resolution	Lower Limit (ps)	Upper Limit (ps)
1 μeV	70	7000
25 μeV	2	250
100 μeV	0.7	70

Elastic windows measurements differ from time of flight (ToF) measurements, which use peak fitting to separate the elastic component (structural OH) of the spectra from the quasi-elastic (water) component.

Previously we compared interparticle water with interlayer water. In this new work we planned to examine the cation interaction with interlayer water as a function of (1) cation, (2) layer charge and (3) with different amounts of water in the interlayer. The measurements presented here focus on the water cation interactions in Na and Ca saturated SAz-1 equilibrated at P/Po of 0.54 over saturated

$Mg(NO)_3 \cdot 6H_2O$ solution. Two types of spectra were measured: (1) "loss of water" spectra were measured and spectra recorded every hour over 24 hours in special cans that allowed water to escape from the clay and (2) "water constant" spectra where the measurements were made in sealed cans over 12 hours. The QENS time of flight (ToF) spectra were measured with a resolution of 98 μeV at the Helmholtz-Zentrum Berlin für Materialien und Energie in the Berlin ToF spectrometer NEAT using the experimental procedure reported by Bordallo et al. (2008) except for the omission of thin Teflon. The "water constant" data was grouped into three ranges of Q and fit to three peaks: (1) the resolution Gaussian (where the peak width was constrained to be the same as that of vanadium), (2) a narrow Lorentzian peak (QE1) and (3) a broad Lorentzian peak (QE2) with the fitting parameters shown in Table 2.

Table 2. Fitting parameters for "water constant" data.

Na-SAz-1	Q = 0.54	Q = 1.07	Q = 1.52	Q = 1.89	Q = 2.19
Elastic Intensity (fit height)	13.2	9.1	7.6	4.1	1.5
QE1 Intensity (fit height)	0.672	0.916	1.125	1.221	0.995
QE2 Intensity (fit height)	0.358	0.248	0.189	0.105	0.055
Elastic Area (fit %)	80.1	61.2	54.0	45.0	33.4
QE1 Area (fit %)	8.0	23.4	30.4	40.0	50.2
QE2 Area (fit %)	11.9	15.4	15.5	15.0	16.4
QE1 Line width (fit half width)	0.062	0.127	0.134	0.112	0.087
QE2 Line width (fit half width)	0.118	0.331	0.451	0.570	0.617

Ca-SAz-1	Q = 0.54	Q = 1.07	Q = 1.52	Q = 1.89	Q = 2.19
Elastic Intensity (fit height)	12.0	6.2	4.6	2.4	1.0
QE1 Intensity (fit height)	1.23	1.75	1.75	1.61	0.923
QE2 Intensity (fit height)	0.332	0.409	0.412	0.213	0.059
Elastic Area (fit %)	74.0	50.7	42.2	31.6	27.8
QE1 Area (fit %)	20.0	34.8	34.3	44.5	56.1
QE2 Area (fit %)	5.9	14.5	23.4	23.9	16.0
QE1 Line width (fit half width)	0.084	0.081	0.074	0.079	0.086
QE2 Line width (fit half width)	0.092	0.146	0.223	0.343	0.423

The "loss of water" spectra were fitted to a resolution function and to a single Lorentzian curve from data grouped into one Q range. This difference from the "water constant" spectra was because there were insufficient counts in one hour spectra. It was known that at 0.54 P/Po the calcium saturated smectite contained 172 mg(H_2O) / g(dry clay) while the Na saturated clay contained 161 mg(H_2O) / g(dry clay). From the loss of intensity of the total water signal it was possible to estimate the amount of water left in the clay and this was plotted against both the half width of the quasi-elastic line and the quasi–elastic fraction (which is the ratio of the area of the single Lorentzian to the total area). (See Figs. 3 and 4.). When less than ~145mg/g of water remains it appears that hydration shell water is being held more tightly to Ca than in Na, which continued to lose water and to have significantly less peak width after this limit.
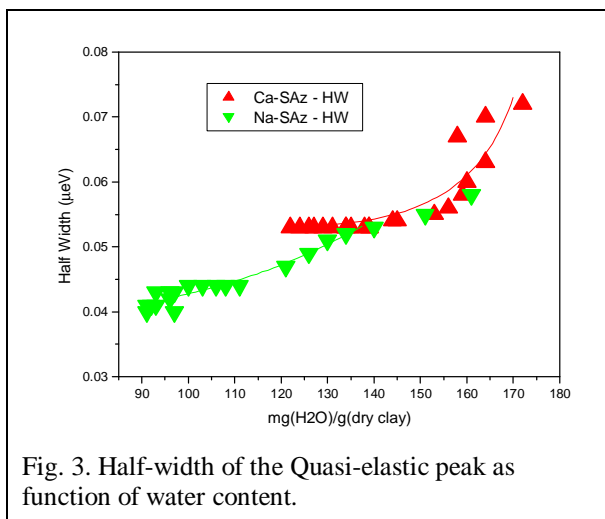
Fig. 3. Half-width of the Quasi-elastic peak as function of water content.
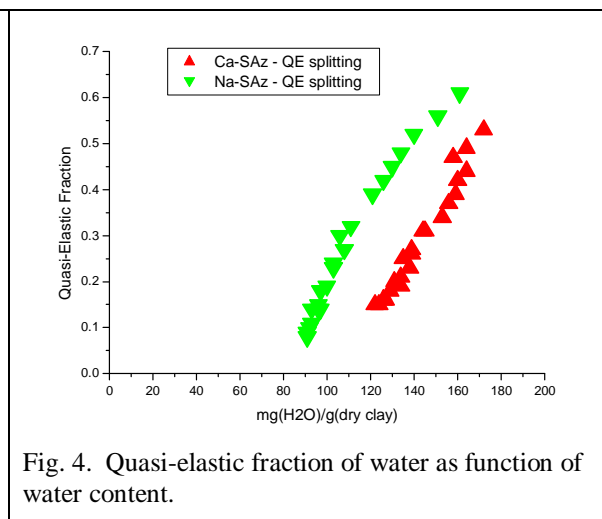
Fig. 4. Quasi-elastic fraction of water as function of water content.

We are also fitting these spectra to see if it is possible to decouple the translational motion from the rotational motion of the water as was carried out in the previous paper. We have, from this work, and the previous work, concluded that neutron scattering does have the capability to distinguish between three types of water in clays (a) interparticle (or external) water (b) interlayer water in the cation hydration shell (c) and interlayer water outside the cation hydration shell. We are carrying out an additional investigation to ensure that the magnetic structure of the clay does not contribute a systematic error to the measurement of quasi-elastic spectra as our previous work showed that the magnetic structure of clay gave measurable signals in the quasi-elastic region. While our interpretation may be regarded as a somewhat basic the work illustrates the utility of neutron scattering to study the clay-water interactions and the advantages derived from the capability of directly relating the number of neutrons to the amount of water. In future work we plan to measure these clays at different ranges of P/Po and to use charge-reduced clays.

References

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