Procedure for Cation Exchange Capacity and *Cation Fixation Capacity*

1. In a pre-weighed centrifuge tube (m_T) containing a known amount of clay sample (m_s), saturate the clay with the exchanged cation by adding a 1 N solution of MCl (actually, if problems develop we could switch to the NO_3^- anion) and stir 24 h or over night. Wash 5 times with the 1 N solution, stirring vigorously after each wash. Each washing should be centrifuged so as to obtain a clear supernatant.

    m_T = mass of centrifuge tube with cap

    m_s = mass of clay sample

2. Wash 5 times, to a clear supernatant each time, with 10^{-3} N solution of the same salt solution. Save the last supernatant to determine the concentration of M^+ (C_i) in the sample, and weigh the decanted tube+sample+solution (m_j) to obtain the remaining solution volume (V_i). Calculate the number of moles of M^+ remaining in the sample (M_i) by $V_i * C_i$.

    C_i = concentration of entrained solution in sample after initial cation saturation

    m_j = mass of tube + sample + solution = m_T + m_s + V_i (assumes the solution has a density of 1.0)

    V_i = volume of entrained solution in sample after initial cation saturation

    $V_i = m_j - m_T - m_s$

    M_i = moles of saturating cation remaining in the sample but NOT on the exchange complex after initial cation saturation

    $M_i = V_i \cdot C_i$

3. Refill the centrifuge tube with the exchanger solution, consisting of either 1 or 0.5 N $MgCl_2$, resuspend thoroughly by vortexing vigorously while filling and for about 0.25 h after filling until suspension is very well mixed. Centrifuge until clear, decant and save supernatant, and repeat five times. Supernatants can be combined (see step 4 if fixed cation is to be determined).

4. *If the amount of fixed cation is to be determined, save the final supernatant separately and determine its concentration with respect to M^+ (C_{fl}). Weigh the sample + tube + solution (m_{fl}), calculate the volume of entrained solution (V_{fl}), and calculate the amount of M^+ remaining in the sample but NOT on the exchange complex (M_{fl}).*

    c_{fl} = *Concentration of exchanged cation in the final supernatant after exchange with exchanger cation ($MgCl_2$).*

    m_{fl} = *mass of sample + tube + remaining solution after exchange with the exchanger cation and final decant*

$v_{f1} =$ Volume of solution remaining in sample after final decant from the exchange procedure.

$$v_{f1} = m_{f1} - m_T - m_s$$

$M_{f1} =$ moles of exchanged cation remaining in the entrained solution after exchange with the exchanger cation and after the final decant, but that is NOT on the exchange complex. This value is expected to very small.

$$M_{f1} = V_{f1} \cdot C_{f1}$$

5.   To complete the cation exchange capacity measurement, weigh the combined supernatant solution that was collected during the exchange process (V_{f2}) and measure its concentration with respect to M^+ (C_{f2}). Calculate the moles of M^+ that were removed from the sample through the exchange process (M_{f2}).

$V_{f2} =$ Volume of combined supernatant solutions obtained from the exchange procedure.

$C_{f2} =$ Concentration of exchanged cation in all of the collected supernatants after exchange with exchanger cation ($MgCl_2$).

$M_{f2} =$ Moles of M^+ exchanged from the clay complex.

$$M_{f2} = V_{f2} \cdot C_{f2}$$

6.   Calculate the cation exchange capacity by dividing the number of moles exchanged (M_{f2}) by the mass of clay (m_s).

$$CEC = \frac{M_{f2}}{m_s} \text{ (Units will be moles/g clay)}$$

If the value of M_{f1} is more than 1% of M_{f2}, the correction should be applied.

7.   *To complete the determination of fixed M^+, digest the clay gel remaining after the final decant in step 4 above. Measure the concentration of M^+ in the digestate (C_{fixed}), and calculate the amount of fixed M^+ from the expression*

$$M_{fixed} = \frac{C_{fixed} \cdot V_{fixed} - M_{f1}}{m_s}$$

where v_{fixed} is the total volume of the analyte solution (including account for dilution factors). The value of M_{f1} should be very small and may be neglected after first verifying this fact.