



## Abstract

The cation exchange capacity (CEC) of clay minerals is a fundamental property. During formation, clays undergo isomorphous substitution resulting in a net negative charge, corresponding to the number of cations required to balance the charge; this is the CEC. The CEC of four standard clays has been determined using three different methods: ammonia gas sensing ion selective electrode (ISE), ultra-violet visible light spectrophotometry (UV-vis), and atomic absorption spectrophotometry (AA). UV-vis and AA determination methods rely on measuring the absorbance of the cations remaining in solution after exchange with the clay. The ISE method of determination relies on the exchange of ammonium cations through the saturation of the exchangeable cation sites in the layers. Comparison of the three methods on hectorite clay from California, and montmorillonite clays from Texas, Wyoming, and Arizona was done to determine the accuracy of the three individual methods. The UV-vis method was performed on clays exchanged with  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$ . The AA method was performed on clays exchanged with  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ . The CEC of the four clays was determined via all three methods and the results compared back to the literature values. The three methods appear to be equally poor for making accurate measurements of the CEC; however, UV-vis and AA seem to be the most precise across the board.

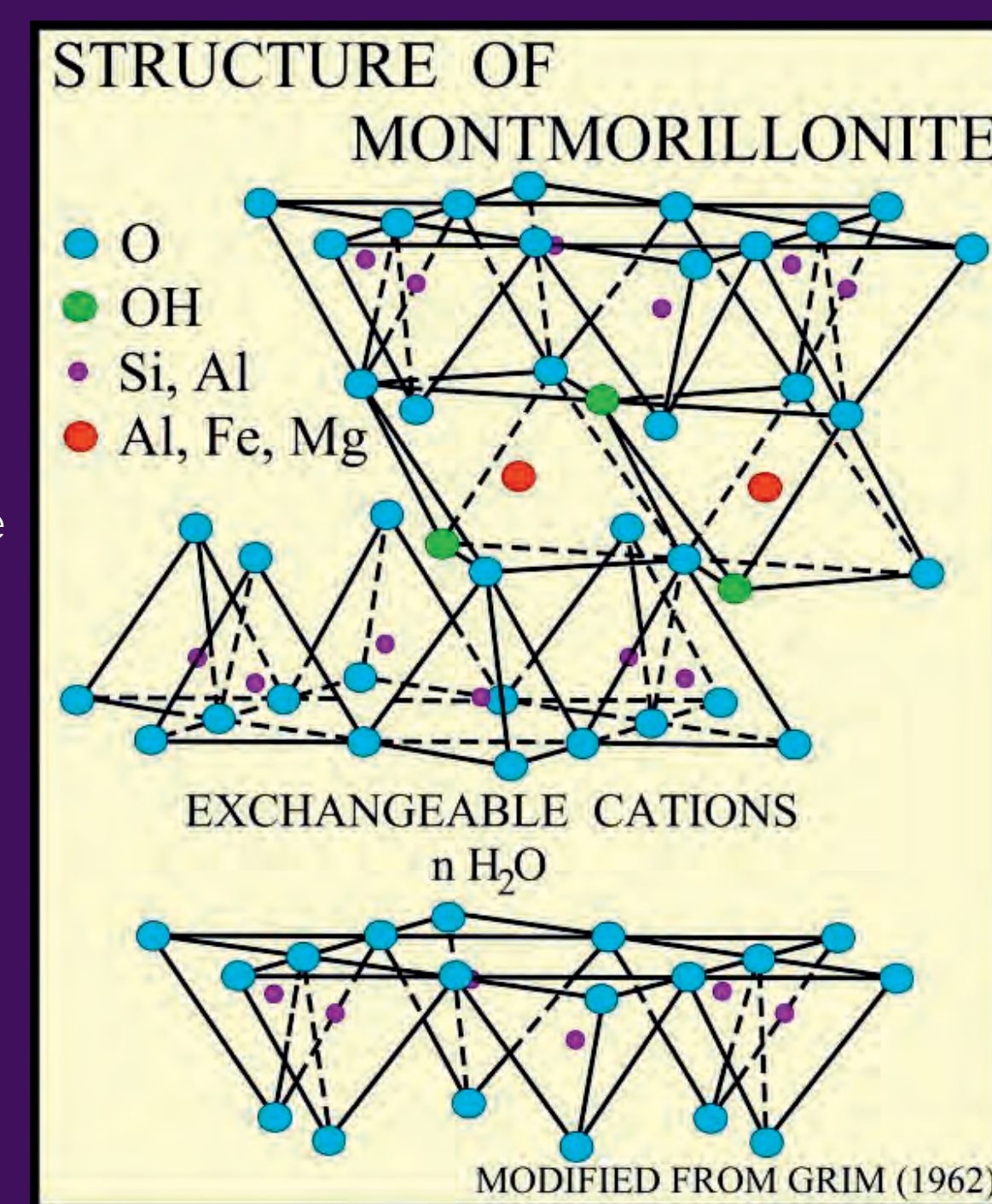


Figure 1. Structure of a montmorillonite clay.

pubs.usgs.gov/of/2001/of01-041/html/docs/images/monstru.jpg

## Method

Clay was purified in an eight step process. Sedimentation removed non-clay impurities and allowed only clay to be processed. Decarbonation and metal removal allowed for the isolation of clay from carbonates and metals on the surface of the clay. Oxidation was followed by exchange to sodium, and then clay was put through dialysis to remove excess ions. Finally clay was dried.

**Ammonia Electrode Method:** Dried sodium clay was exchanged with ammonium chloride to 200% saturation and put in dialysis to remove excess ions. The ammonium clay was then dried. Data consists of 5 measurements per data set. Standards were created from serial dilutions of 0.10M ammonium chloride. A 10M sodium hydroxide solution was used to cause reaction. The ammonia generated via reaction was monitored using an ammonia electrode.  $\text{NH}_4\text{-clay} + \text{NaOH}_{(aq)} \rightarrow \text{NH}_3(g) + \text{H}_2\text{O} + \text{Na-clay}$

**Spectroscopic Method:** Suspensions of the clays were prepared with copper (II) and nickel (II) to 150% excess of the CEC for SAz-1. The suspensions were allowed to mix overnight. The clays were allowed to settle and samples of the supernatant were collected and filtered using a 0.45 micron filter. The resulting supernatants were analyzed using UV-Vis and AA. Standards were prepared for UV-Vis using copper (II) chloride and nickel (II) chloride. Standards for the AA were made using a 1000ppm copper and nickel standard.

## Results

Ammonia Gas ISE Method				
Clay Type	SHCa-1	SWy-2	STx-1b	SAz-1
Accepted CEC (meq/100 g)	44	80	88	120
Trial 1	51.99	38.93	36.41	70.33
% Error	18.16	51.34	58.63	41.39
Trial 2	49.73	57.53	74.54	131.9
% Error	13.02	12.09	15.3	9.917
Trial 3	n/a	84.74	57.56	158.9
% Error		5.925	34.59	32.42
Trial 4		78.66	n/a	n/a
% Error		1.675		
Trial 5		93		
% Error	16.21			

UV Vis Method				
Clay Type	SHCa-1	SWy-2	STx-1b	SAz-1
Accepted CEC (meq/100 g)	44	80	88	120
$\text{Cu}^{2+}$	83.7	111.4	42.8	121.9 99
% Error	90.2	39.25	51.4	1.583 17.5
$\text{Ni}^{2+}$	119	-15.38	109.1	113
% Error	170.5	80.78	24	5.833

AA Method				
Clay Type	SHCa-1	SWy-2	STx-1b	SAz-1
Accepted CEC (meq/100 g)	44	80	88	120
$\text{Cu}^{2+}$	293.8	41.9	293.4	131.6 293.9
% Error	567.8	52.4	233.4	9.67 144.9
$\text{Ni}^{2+}$	63.9	76	94	113.2
% Error	45.2	5	6.82	5.67

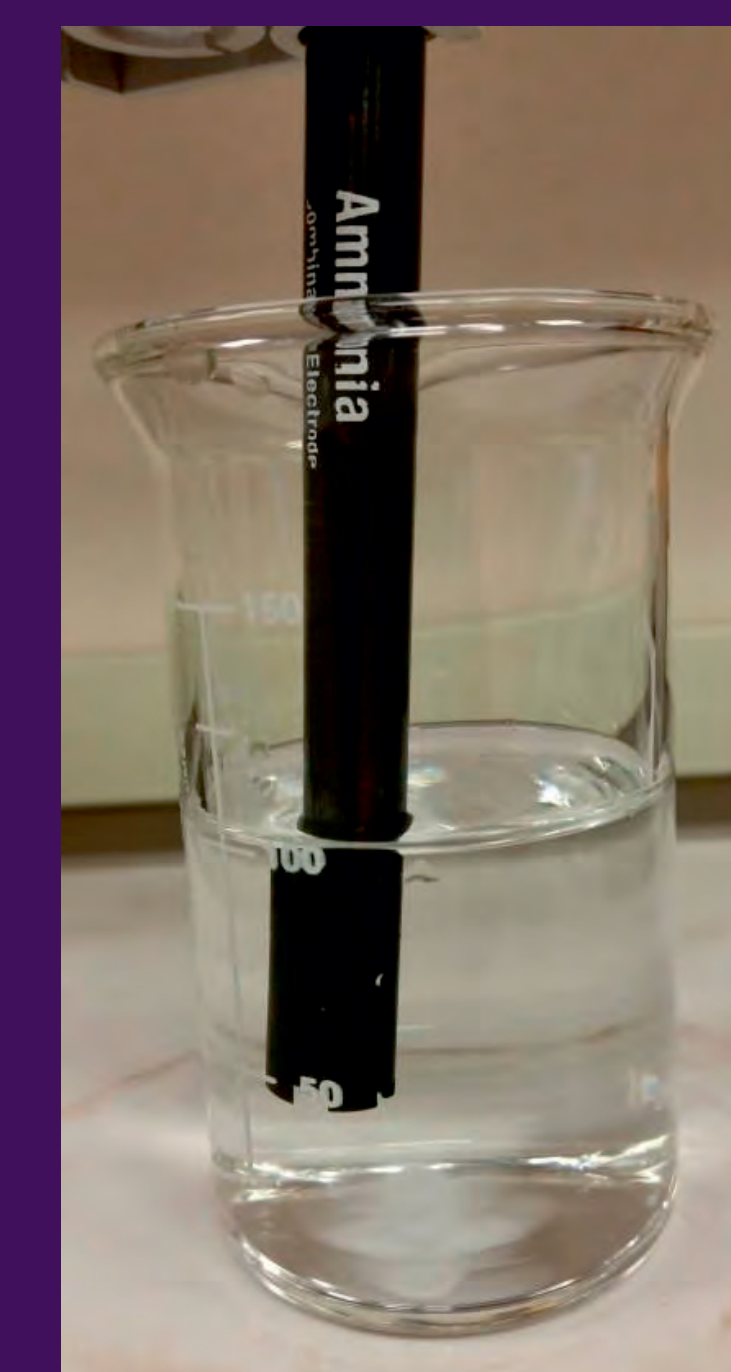


Figure 2. Ammonia gas electrode method.

## Conclusions

**Ammonia Electrode Method:** The results obtained using the ammonia electrode method are very inconsistent. Much of the variance seen in the results is due to the equipment itself. If the membrane on the end of the electrode starts to deteriorate, the sodium hydroxide solution can cause the internal ammonium fill solution to convert to ammonia and be detected as well. While the membrane can be changed, it is often difficult to determine when this should be done.

**Spectroscopic:** The results obtained using the UV-Vis and AA are encouraging. Overall, the exchange with copper(II) generated results closest to the accepted CEC and with low variance initially. However, further testing with the 150% excess metal resulted in results with high variance far out of range. Likely this is due to the adsorptive properties of the clays.

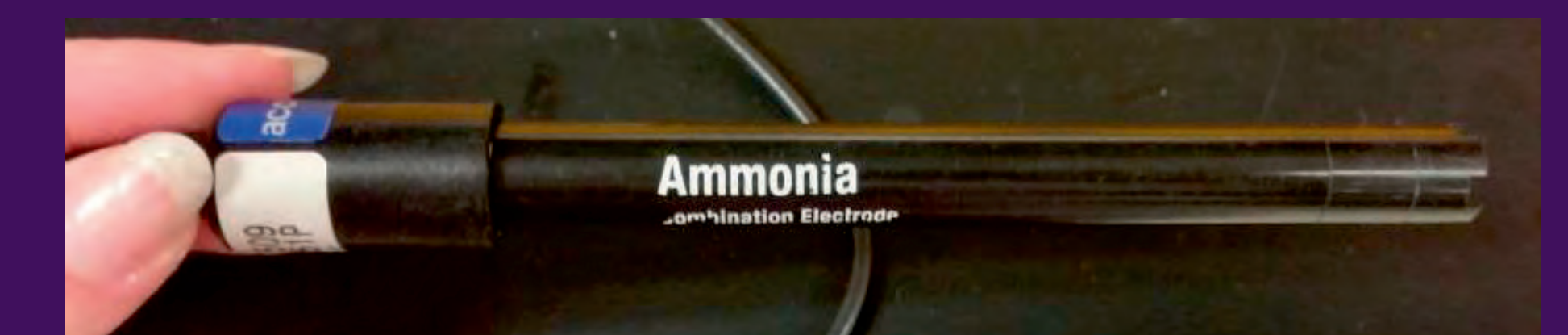


Figure 3. Accumet ammonia gas electrode.



Figure 4. Clays in metal exchange.

## Future Research

Spectroscopic analyses will be repeated, utilizing 5 samples from each exchange and utilizing cobalt (II) chloride.

Ammonia gas sensing electrode method will be repeated by creating a uniform particle size and enclosing the system to reduce the loss of ammonia gas during the reaction.

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## References

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