Cation Exchange: What it is, how it is measured, and does it matter?

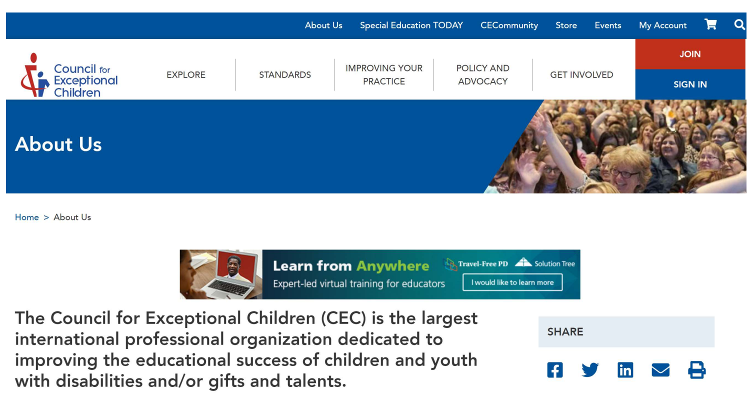
Tom DeSutter

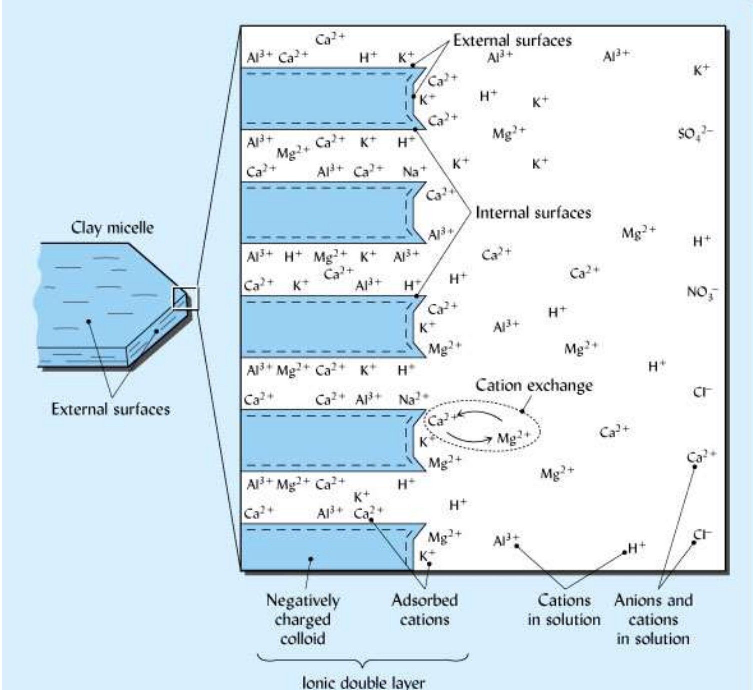
2021 Soil and Soil/Water Workshop

20 January 2021

One home, 2 CEC's

The capacity of soil to hold nutrients for plant use. Specifically, CEC is the amount of negative charges available on clay and humus to hold positively charged ions.
-NRCS





Brady and Weil

What is *Cation Exchange*?
Formal definition: “The interchange between a cation in solution and another cation in the boundary layer between the solution and surface of negatively charged material such as clay or organic matter” – Glossary for Soil Science Terms

Nature of cation exchange

- **A simple electrostatic attraction, not a strong “binding” by the soil**
- **Ions constantly exchanging with cations in the soil solution**
- **Ions held by cation exchange readily re-supply the soil solution**
- **Ions held by cation exchange, not readily leached from soil**

Most clay minerals are electrically "charged"

- Most clays have a NEGATIVE charge associated with them
- These negative charges are neutralized by exchangeable cations
  - One of the most important concepts of soil chemistry and soil fertility
  - "This process is important because many plant nutrients, including potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), ammonium (NH^{4+}), zinc (Zn^{2+}), and iron (Fe^{3+}) are cations held to soil by the CEC." R. Fergusen

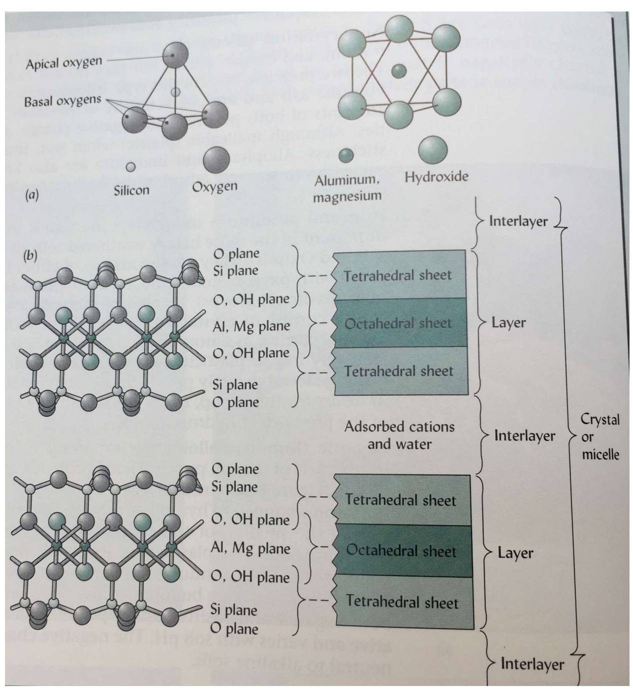
Where do these negative charges come from?

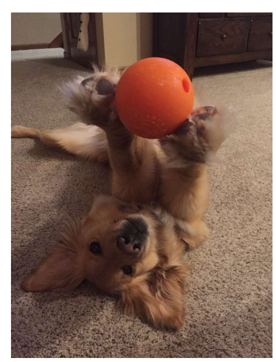
- Isomorphic substitution in aluminosilicate clays
- Broken bonds on the edges of clays, oxide minerals
- Organic matter has negative charges, from ionization of organic groups

Isomorphic substitution

- Iso = same
- Morphic = shape

- There are substitutions in the chemical structure of aluminosilicate clays that do not alter the shape of the clay

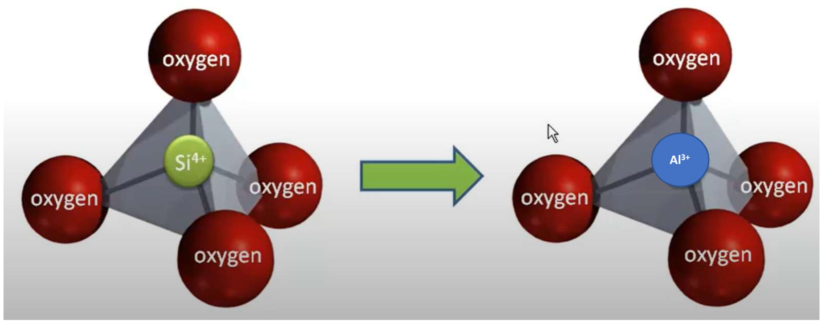




Brady and Weil

Isomorphic substitution

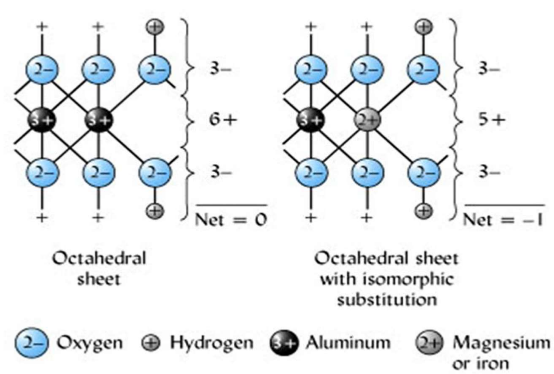
- In the Silicon-tetrahedral layer
  - Al^{3+} substitution for Si^{4+}
    - A negative charge is left over

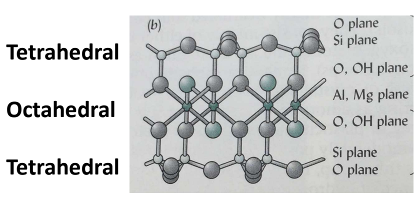


H. Dolliver

Isomorphic substitution

- In the Aluminum-octahedral layer
  - Mg^{2+} or Fe^{2+} for Al^{3+}
    - A negative charge is left over





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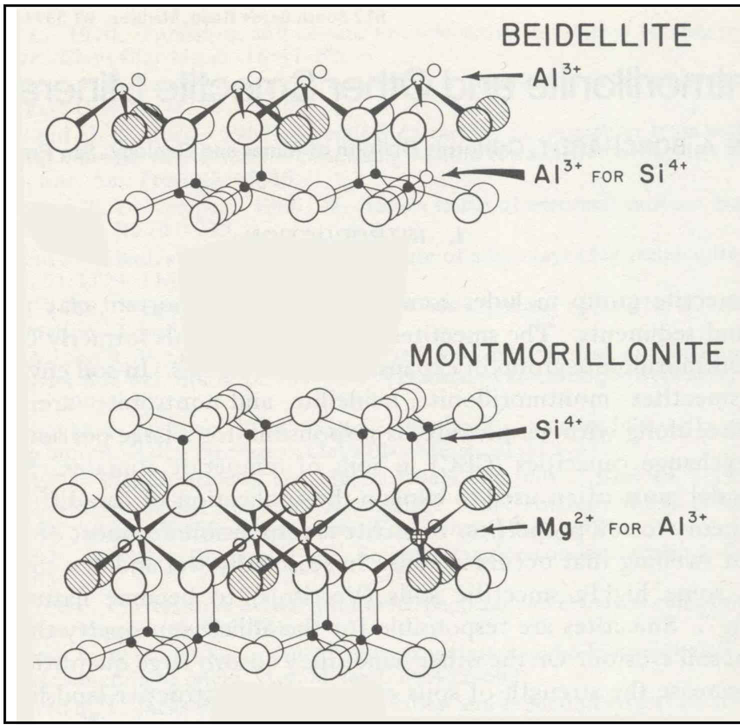
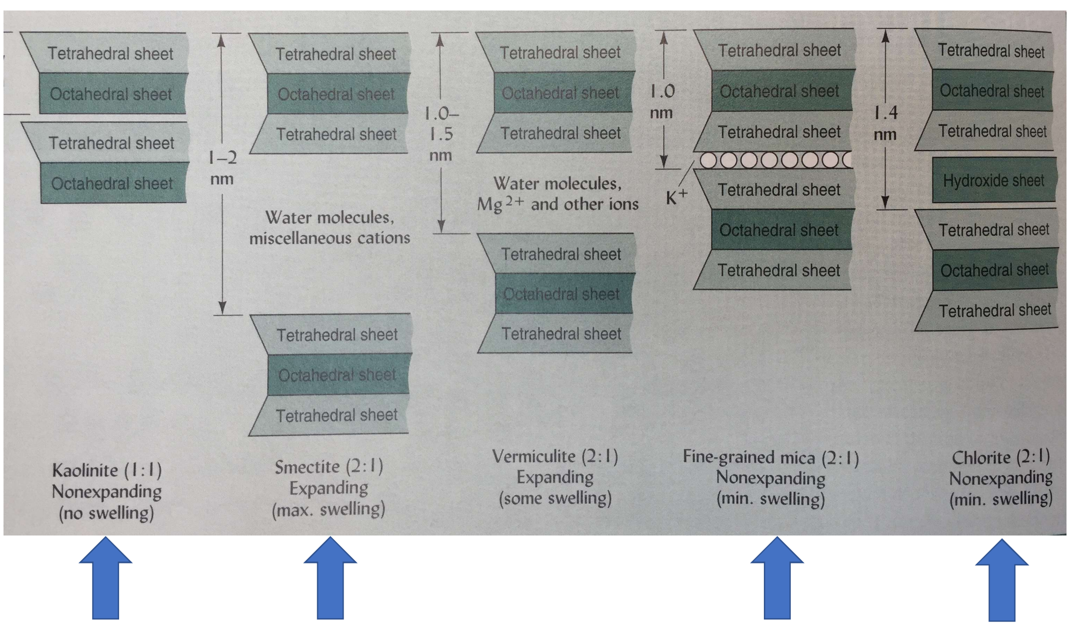


Beidellite is a smectite-type mineral found in North Dakota soils

Montmorillonite being the most common smectite-type clay in our area



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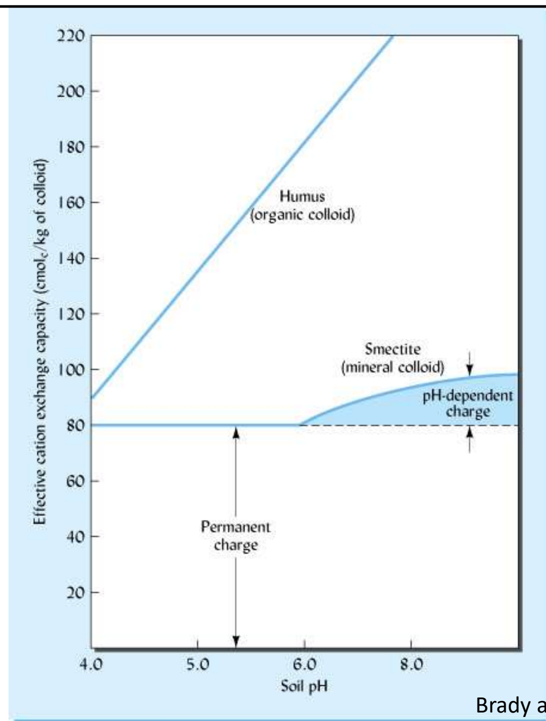
"Permanent charge"

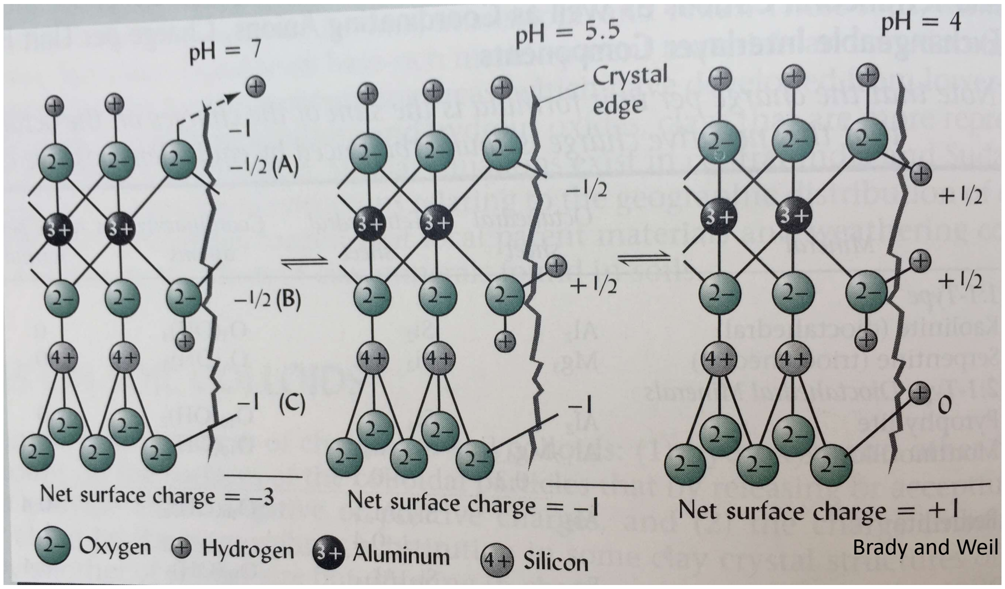
- Isomorphic substitution results in a fixed, or permanent charge on clays
- Permanent charge is not influenced by soil pH

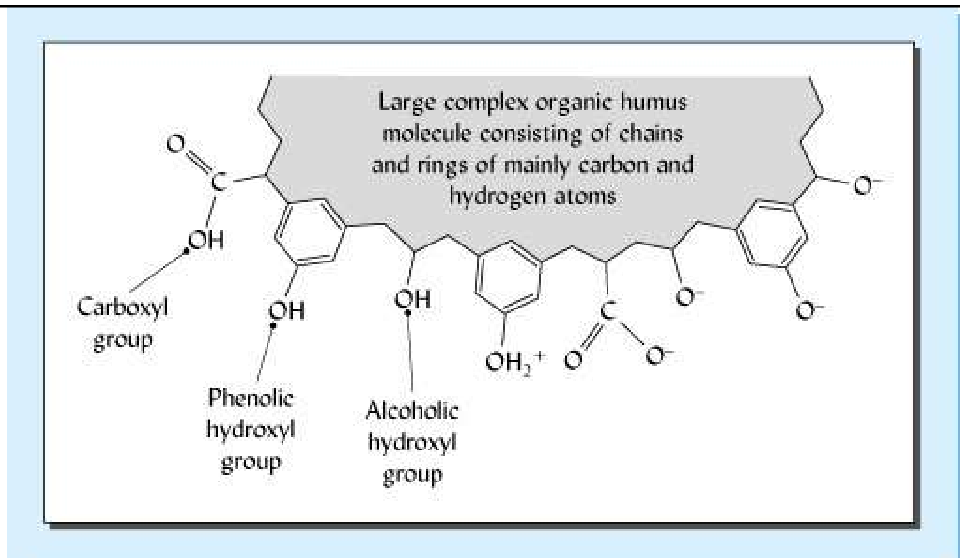
Permanent and pH dependent charge



Brady and Weil

Kaolinite pH dependent charges, broken edges





Brady and Weil

How do we define this property?

- How do we define the number of negative charges in a gram of clay or soil?
- Term is <u>cation exchange capacity</u>, a very important soil chemical property
- Modern units of quantification are $cmol_c$/kg but meq/100g of soil is still used by soil testing laboratories.
  - NOTE: for gypsum requirement app the units are $mmol_c$/kg

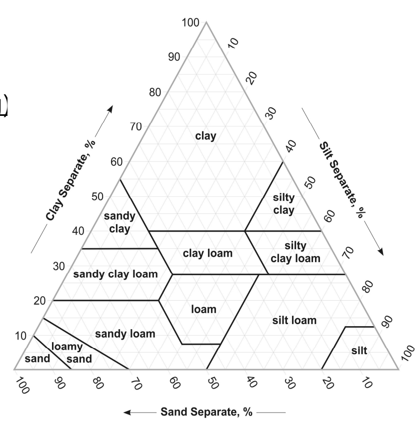
Element	Atomic wt.	Valence	Eq per mole	Eq wt.	Divide ppm (mg/kg) from your soil test report by "X" to get meq/100g or $cmol_c$/kg
	g/mol	"+" charges/ion	Eq/mol	g/eq	"X"
Na	23	1	1	23	230
K	39	1	1	39	390
H	1	1	1	1	10
Ca	40	2	2	20	200
Mg	24	2	2	12	120
Al	27	3	3	9	90

NOTE:
-Equivalent wt = atomic wt/valence
So, for Ca^{2+}, 40 g per mol/2Eq Ca^{2+} per mol = 20 g/Eq of Ca^{2+}
-1Eq = 100 $cmol_c$ = 1 mol_c

Estimating CEC by Texture

Generalized soil texture:CEC relationship

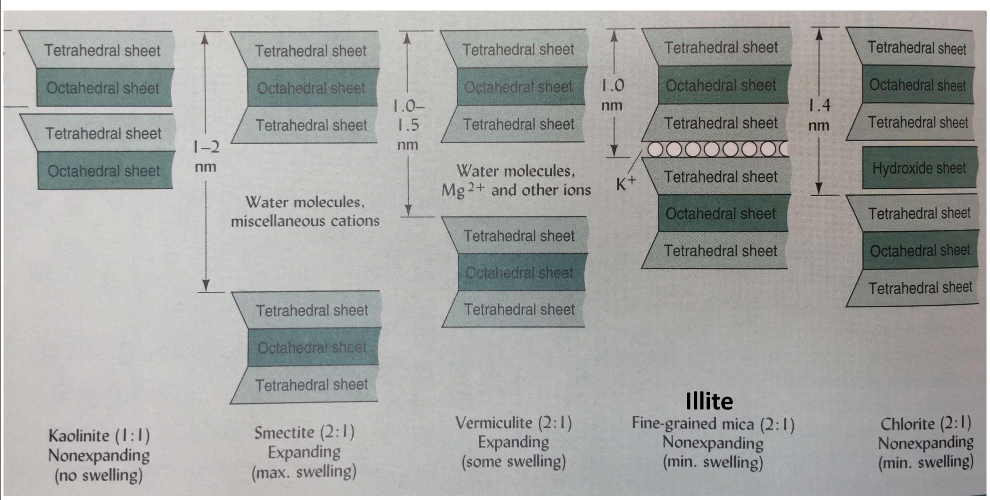
Soil Texture	Approximate CEC (meq/100g)
organic	50-100
clay loam	20-30+
silt loam	15-20
loam	12-15
sandy loam	10-12
loamy fine sand	less than 10

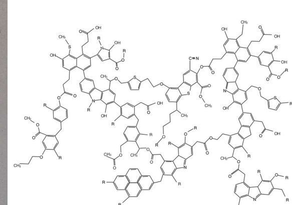


Example 1: For a soil having a clay loam texture what is the range of CEC for this soil?

Answer: **between <u>20-30+ meq/100g</u>**

Remember that:
- Sandy loam (1/4" ribbon is about 10% clay)
- Loam (1" ribbon is about 20% clay)
- Clay loam (2" ribbon is about 35% clay)





10 meq/100g **100 meq/100g** **30 meq/100g** **30 meq/100g** **200 meq/100g**

DOI: 10.3390/life8020018

Brady and Weil

Estimating CEC by Knowledge of Clay Component

Soil Component	Approximate CEC (meq/100g or $cmol_c/kg$)
Soil organic matter	200
Smectite	100
Illite	30
Chlorite	30
Kaolinite	10

Example 2. If you determined, using the hydrometer method, that the clay content of a soil was 25% (0.25 kg clay/kg soil) and that this soil also had a soil organic matter (OM) content of 5% (0.05 kg OM/kg soil), what is its estimated CEC? NOTE: assume that clay fraction is dominated by smectite.

For clay: $\frac{100\ cmol_c}{kg\ clay} \times \frac{0.25\ kg\ clay}{kg\ soil} = \frac{25\ cmol_c}{kg\ soil}$

For OM: $\frac{200\ cmol_c}{kg\ OM} \times \frac{0.05\ kg\ OM}{kg\ soil} = \frac{10\ cmol_c}{kg\ soil}$

***Answer*: The sum of each of these fractions is the estimated CEC of this soil: 25 + 10 = 35 meq/100g**

Detailed clay mineralogy

Activation Laboratories Ltd. A19-11222

Table 1. Mineral abundances in bulk samples (wt %)

Client ID	#101	#102	#103	#104	#105	#106	#107
Actlabs ID	A19-11222-1	A19-11222-2	A19-11222-3	A19-11222-4	A19-11222-5	A19-11222-6	A19-11222-7
Quartz	26.3	36.0	37.3	52.7	33.6	67	52.6
Plagioclase	5.7	8.8	7.7	15.4	6.0	9.1	15.1
K feldspar	3.1	6.0	5.0	4.7	3.8	5.4	5.5
Muscovite/Illite	4.0	2.4	3.1	4.9	6.4	1.6	1.3
Kaolinite	1.0	1.0	0.5	0.6	1.1	trace	trace
Chlorite	trace	trace	0.5	0.5	2.1	trace	trace
Smectite*	12	12	7	10	21	4	3
Amphibole	n.d.	n.d.	1.2	n.d.	n.d.	n.d.	1.0
Heulandite	0.3	n.d.	n.d.	n.d.	n.d.	0.3	n.d.
Dolomite	n.d.	1.1	0.9	n.d.	5.9	n.d.	n.d.
Calcite	n.d.	n.d.	0.7	n.d.	3.1	n.d.	n.d.
Amorphous	47.6	32.7	36.1	11.2	17.0	12.6	21.5

Note: n.d. = not detected; *the amount of smectite is a rough estimate calculated from the relative proportions of smectite and illite in the < 2 μm size fraction

Table 2. Relative proportions of clay minerals in the < 2 μm size fraction

Client ID	#101	#102	#103	#104	#105	#106	#107
Actlabs ID	A19-11222-1	A19-11222-2	A19-11222-3	A19-11222-4	A19-11222-5	A19-11222-6	A19-11222-7
Smectite	70	81	65	62	66	68	69
Illite	24	15	28	30	20	26	26
Kaolinite	4	4	4	4	5	4	3
Chlorite	2	trace	3	4	9	2	2

Example. This soil had a clay content of 11% (= 0.11 kg clay/kg soil). <u>The %OM of this sample was 0.5%.</u>

Clay mineral	Assumed level (meq/100g or $cmol_c$/kg)	Amount (% of the soil's clay content)
Smectite	100	63 (= 0.63 kg smectite/kg clay)
Illite	30	27
Chlorite	30	5
Kaolinite	10	5
Organic Matter	200	

What is its estimated CEC?

$$smectite: \frac{0.11\ kg\ clay}{kg\ soil} \times \frac{0.63 kg\ smectite}{kg\ clay} \times \frac{100\ cmol_c}{kg\ smectite} = 6.9\ \frac{cmol_c}{kg\ soil}$$

$$illite: \frac{0.11\ kg\ clay}{kg\ soil} \times \frac{0.27 kg\ illite}{kg\ clay} \times \frac{30\ cmol_c}{kg\ illite} = 0.9\ \frac{cmol_c}{kg\ soil}$$

$$chlorite: \frac{0.11\ kg\ clay}{kg\ soil} \times \frac{0.05 kg\ chlorite}{kg\ clay} \times \frac{30\ cmol_c}{kg\ chlorite} = 0.2\ \frac{cmol_c}{kg\ soil}$$

$$kaolinite: \frac{0.11\ kg\ clay}{kg\ soil} \times \frac{0.05 kg\ kaolinite}{kg\ clay} \times \frac{10\ cmol_c}{kg\ kaolinite} = 0.06\ \frac{cmol_c}{kg\ soil}$$

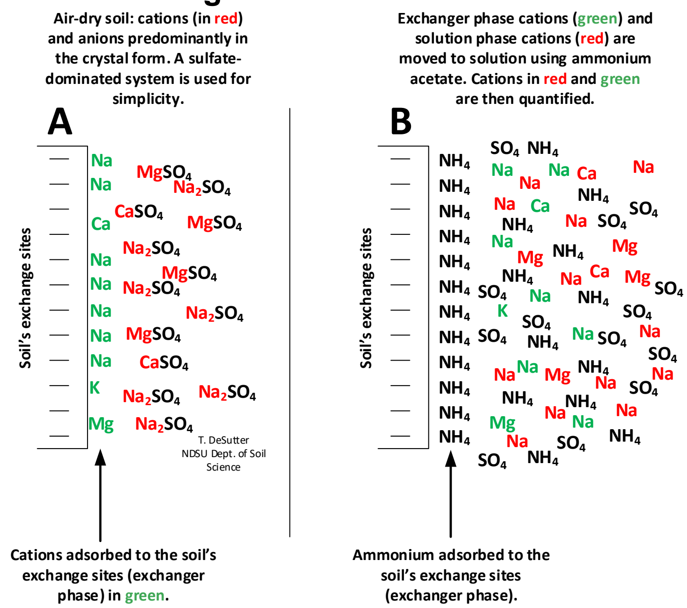
$$organic\ matter: \frac{200\ cmol_c}{kg\ OM} \times \frac{0.005\ kg\ OM}{kg\ soil} = 1.0\ \frac{cmol_c}{kg\ soil}$$

Answer: **The sum of each of these fractions is the estimated CEC of this soil: 6.9+0.9+0.2+0.06+1.0=<u>9.1 meq/100g.</u> This soil is actually from a gravel road from Dunn County (ND; north of Dickinson).**

Let's talk about getting CEC

- **Summation**
  - **When soils have soluble salts, exchanger and salt cations are summed**
  - **This is then termed as 'extractable cations'**
- **NH_4-K**
  - **NH_4 is added to the exchange sites and then removed by K, NH_4 then quantified**
  - **This is termed as 'exchangeable cations'**

The summation method used to determine extractable cations. Commonly done at most soil testing laboratories.

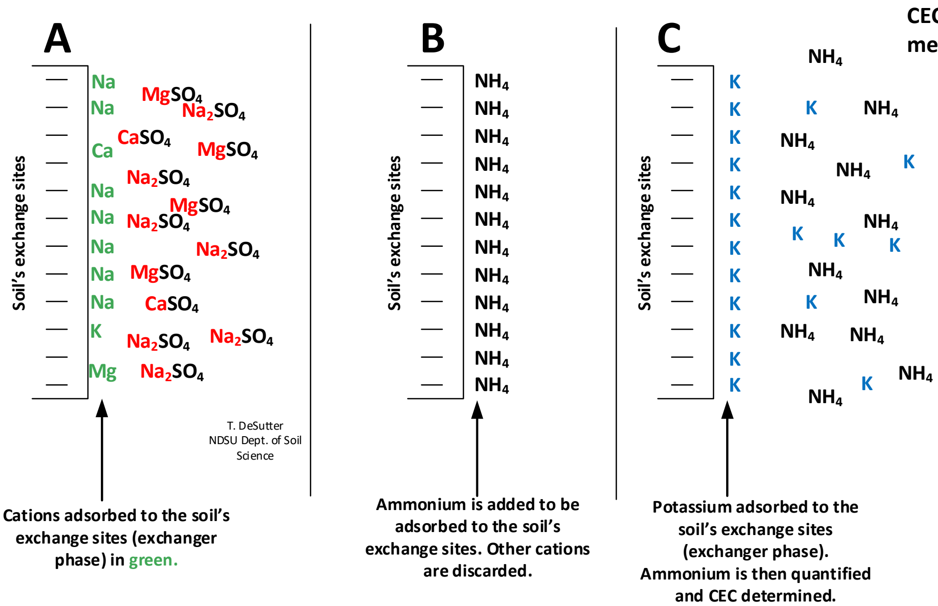


Summation method:

CEC = sum of the red and green cations (units of meq/100g or cmol$_c$/kg)

This would be termed "extractable cations"

Determination of CEC using the replacement of one cation (NH_4^+) with another cation (K^+). True method of determining CEC, although not commonly done in soil testing laboratories.



CEC = sum of NH_4^+ (units of meq/100g or cmol$_c$/kg)

This would be termed "exchangeable cations"

Element	Atomic wt.	Valence	Eq per mole	Eq wt.	Divide ppm (mg/kg) from your soil test report by "X" to get meq/100g or $cmol_c/kg$
	g/mol	"+" charges/ion	Eq/mol	g/eq	"X"
Na	23	1	1	23	230
K	39	1	1	39	390
H	1	1	1	1	10
Ca	40	2	2	20	200
Mg	24	2	2	12	120
Al	27	3	3	9	90

NOTE:
-Equivalent wt = atomic wt/valence
So, for Ca^{2+}, 40 g per mol/2Eq Ca^{2+} per mol = 20 g/Eq of Ca^{2+}
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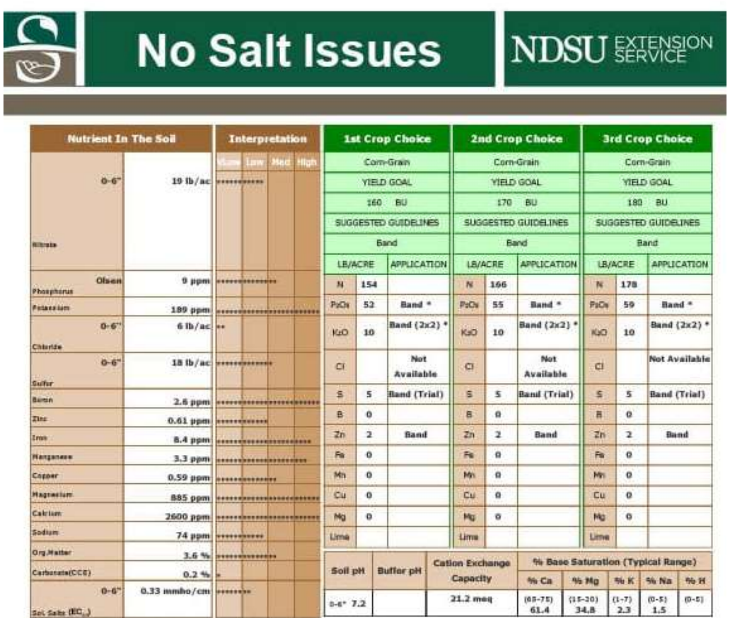


No Salt Issues

NDSU EXTENSION SERVICE

Nutrient In The Soil		
Nitrate	0-6"	19 lb/ac
Phosphorus	Olsen	9 ppm
Potassium		189 ppm
Chloride	0-6"	6 lb/ac
Sulfur	0-6"	18 lb/ac
Boron		2.6 ppm
Zinc		0.61 ppm
Iron		8.4 ppm
Manganese		3.3 ppm
Copper		0.59 ppm
Magnesium		885 ppm
Calcium		2600 ppm
Sodium		74 ppm
Org.Matter		3.6 %
Carbonate(CCE)		0.2 %
Soil Salts ($EC_{1:1}$)	0-6"	0.33 mmho/cm

1st Crop Choice			2nd Crop Choice			3rd Crop Choice		
Corn-Grain			Corn-Grain			Corn-Grain		
YIELD GOAL			YIELD GOAL			YIELD GOAL		
160 BU			170 BU			180 BU		
SUGGESTED GUIDELINES			SUGGESTED GUIDELINES			SUGGESTED GUIDELINES		
Band			Band			Band		
LB/ACRE		APPLICATION	LB/ACRE		APPLICATION	LB/ACRE		APPLICATION
N	154		N	166		N	178	
P_2O_5	52	Band *	P_2O_5	55	Band *	P_2O_5	59	Band *
K_2O	10	Band (2x2) *	K_2O	10	Band (2x2) *	K_2O	10	Band (2x2) *
Cl		Not Available	Cl		Not Available	Cl		Not Available
S	5	Band (Trial)	S	5	Band (Trial)	S	5	Band (Trial)
B	0		B	0		B	0	
Zn	2	Band	Zn	2	Band	Zn	2	Band
Fe	0		Fe	0		Fe	0	
Mn	0		Mn	0		Mn	0	
Cu	0		Cu	0		Cu	0	
Mg	0		Mg	0		Mg	0	
Lime			Lime			Lime		

Soil pH	Buffer pH	Cation Exchange Capacity	% Base Saturation (Typical Range)				
			% Ca	% Mg	% K	% Na	% H
0-6" 7.2		21.2 meq	(65-75) 61.4	(15-20) 34.8	(1-7) 2.3	(0-5) 1.5	(0-5)

So 1,
K: 189/390 = 0.5 meq/100g
Mg: 885/120 = 7.4 meq/100g
Ca: 2600/200 = 13 meq/100g
Na: 74/230 = 0.3 meq/100g

So 2,
For a non-saline soil, using the summation method, the CEC = 0.5 + 7.4 +13 + 0.3 = <u>21.2 meq/100g</u>

So 3,
K: 0.5(100)/21.2 = 2.3%
Mg: 7.4(100)/21.2 = 34.9%
Ca: 13(100)/21.2 = 61.3%
Na: 0.3(100)/21.2 = 1.4%

Saline Soil

NDSU EXTENSION SERVICE

Nutrient In The Soil	Depth	Value
Nitrate	0-6"	81 lb/ac
Phosphorus	Olsen	43 ppm
Potassium		203 ppm
Chloride	0-6"	385 lb/ac
Sulfur	0-6"	120 +lb/ac
Boron		2.9 ppm
Zinc		0.37 ppm
Iron		4.1 ppm
Manganese		2.5 ppm
Copper		0.77 ppm
Magnesium		2553 ppm
Calcium		8652 ppm
Sodium		70 ppm
Org.Matter		3.5 %
Carbonate(CCE)		2.6 %
Sol. Salts ($EC_{1:1}$)	0-6"	4.03 mmho/cm

	1st Crop Choice		2nd Crop Choice		3rd Crop Choice	
	Corn-Grain		Corn-Grain		Corn-Grain	
	YIELD GOAL 160 BU		YIELD GOAL 170 BU		YIELD GOAL 180 BU	
	SUGGESTED GUIDELINES Band		SUGGESTED GUIDELINES Band		SUGGESTED GUIDELINES Band	
	LB/ACRE	APPLICATION	LB/ACRE	APPLICATION	LB/ACRE	APPLICATION
N	81		93		105	
P_2O_5	15	Band (2x2) *	15	Band (2x2) *	15	Band (2x2) *
K_2O	10	Band (2x2) *	10	Band (2x2) *	10	Band (2x2) *
Cl		Not Available		Not Available		Not Available
S	0		0		0	
B	0		0		0	
Zn	5	Band	5	Band	5	Band
Fe	1	Band	1	Band	1	Band
Mn	0		0		0	
Cu	0		0		0	
Mg	0		0		0	
Lime						

Soil pH	Buffer pH	Cation Exchange Capacity	% Base Saturation (Typical Range)				
			% Ca	% Mg	% K	% Na	% H
0-6" 8.1		65.4 meq	(65-75) 66.2	(15-20) 32.6	(1-7) 0.8	(0-5) 0.5	(0-5)

So 1b,

K: 203/390 = 0.5 meq/100g

Mg: 2553/120 = 21.3 meq/100g

Ca: 8652/200 = 43.3 meq/100g

Na: 70/230 = 0.3 meq/100g

So 2b,

For this saline soil, using the summation method, the CEC = 0.5+21.3+43.3+0.3 = 65.4 meq/100g

So 3b,

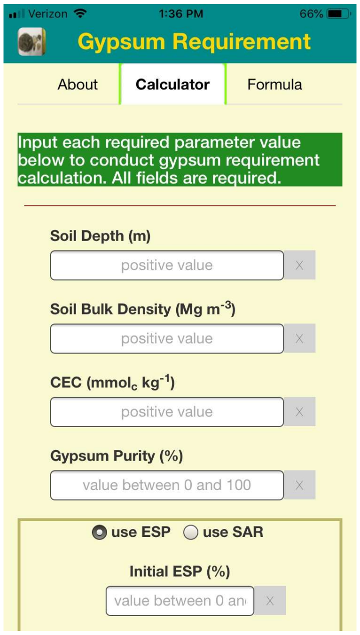
K: 0.5(100)/65.4 = 0.8%

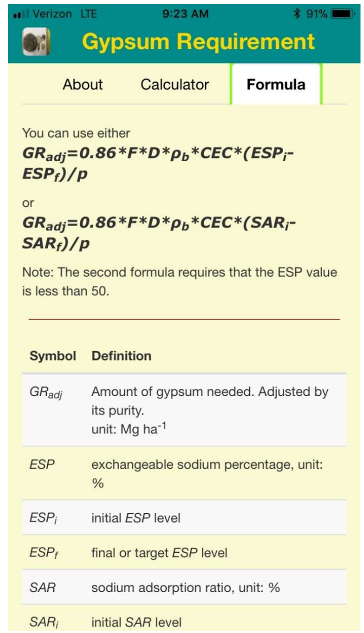
Mg: 21.3(100)/65.4 = 34.9%

Ca: 43.3(100)/65.4 = 66.2%

Na: 0.3(100)/65.5 = 0.5%

How might CEC be used?





Exchangeable Sodium Percentage, ESP

$$ESP = \frac{Na(100)}{CEC}$$

Base Saturation, %BS

$$\%BS = \frac{Na + K + Ca + Mg(100)}{CEC}$$

NOTE: CEC = Na + K + Ca + Mg + H + Al

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A Review of the Use of the Basic Cation Saturation Ratio and the "Ideal" Soil

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The use of "balanced" Ca, Mg, and K ratios, as prescribed by the basic cation saturation ratio (BCSR) concept, is still used by some private soil-testing laboratories for the interpretation of soil analytical data. This review examines the suitability of the BCSR ... pretation of soil analytical data. According to the BCSR concept, maximum plant growth will be achieved only when the soil's exchangeable Ca, Mg, and K concentrations are approximately 65% Ca, 10% Mg, and 5% K (termed the *ideal soil*). This "ideal soil" was originally proposed by Firman Bear and coworkers in New Jersey during the 1940s as a method of reducing luxury K uptake by alfalfa (*Medicago sativa* L.). At about the same time, William Albrecht, working in Missouri, concluded through his own investigations that plants require a soil with a high Ca saturation for optimal growth. While it now appears that several of Albrecht's experiments were fundamentally flawed, the BCSR ("balanced soil") concept has been widely promoted, suggesting that the prescribed cationic ratios provide optimum chemical, physical, and biological soil properties. Our examination of data from numerous studies (particularly those of Albrecht and Bear themselves) would suggest that, within the ranges commonly found in soils, the chemical, physical, and biological fertility of a soil is generally not influenced by the ratios of Ca, Mg, and K. The data do not support the claims of the BCSR, and continued promotion of the BCSR will result in the inefficient use of resources in agriculture and horticulture.

Abbreviations: BCSR, basic cation saturation ratio; CEC, cation exchange capacity.

SSSAJ 71:259-265.

...nificant effect on the earthworm population or on the growth of weeds (grass or broadleaf).

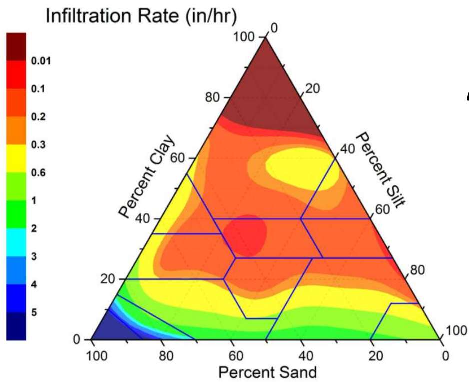
CONCLUSIONS

While the origin of the "ideal" or "balanced" soil concept can be traced back to the late 1800s, it was primarily through work conducted in the 1940s by Bear and coworkers in New Jersey that led to the concept of an "ideal" soil being one with 65% Ca, 10% Mg, and 5% K. Based on this work and on his own work in the 1930s and 1940s, Albrecht promoted the use of the "balanced soil," suggesting that optimal growth will only occur in soils containing the "ideal" composition. It would appear, however, that the soil's chemical, physical, and biological fertility can be maintained across a range of cationic ratios. Indeed, McLean, who worked with Albrecht in Missouri during the 1940s, stated that, on the whole, "there is no 'ideal' basic cation saturation ratio or range" (Eckert and McLean, 1981), and that "emphasis should be placed on providing sufficient, but not excessive levels of each basic cation rather than attempting to attain a favorable basic cation saturation ratio which evidently does not exist" (McLean et al., 1983). The data do not support the claims of the BCSR, and continued promotion of the BCSR will result in the inefficient use of resources in agriculture and horticulture.

https://www.agvise.com/educational-articles/cec-and-holding-n-in-the-soil/

"Cation Exchange Capacity – This is a measurement of holding capacity in your soil. As a rough guideline, we will tell you to multiply 10 times your CEC, and that's the maximum we want in your soil at any one time."

CEC x 10 = what?



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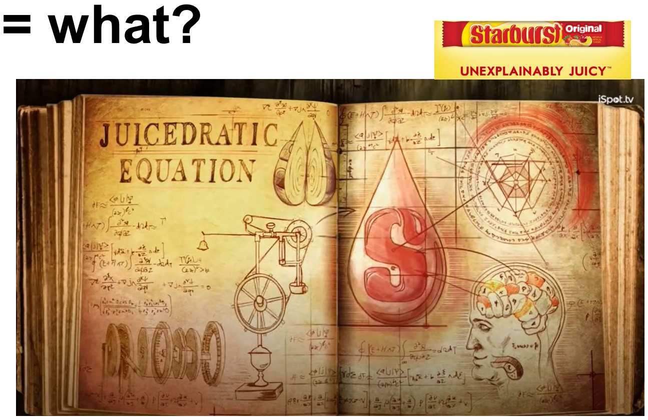

The juicedratic equation can never be proven. It's locked inside a safe, inside a vault, inside a volcano.

-High clay soils and soils with higher organic matter have more binding sites (higher CEC) and can bind more herbicide.
-Increased binding is likely to result in higher application rates being required to achieve a given level of weed control, as less herbicide is available in the soil water for uptake by germinating weeds. Increased binding also generally results in less leaching.
-Conversely, in sandy or low organic matter (lower CEC) soils, there is less binding with more herbicide likely to be available in the soil water. https://grdc.com.au/__data/assets/pdf_file/0036/366867/Pre-emergent-Factors-influencing-the-activity.pdf
-This may lead to increased risk of injury to crops soon after application where there is a lot of freely available herbicide in the soil water, especially for highly soluble herbicides. As a result, many labels recommend a lower application rate in lighter soils.

TABLE 7-1

Influence of cation exchange capacity on soil pH (active acidity), buffer pH (reserve acidity) and lime requirement for three soil textural classes.

Soil Texture	CEC	Soil pH	Buffer pH	Lime Requirement
	meq/100g			*tons per acre*
Loamy sand	6	5.6	6.8	1
Silt loam	14	5.5	6.6	2
Silty clay loam	24	5.6	6.2	4

https://digitalcommons.unl.edu/cgi/viewcontent.cgi?article=2705&context=extensionhist

https://littlefreelibrary.org/

What Plato got wrong about K fertility: Alternative facts.
-Jonas Z. Breker

Beyond selfie-sticks and tours: A quadpeds guide to the real Wyoming.
-Ibee Zeti

A rose within potatoes is like a sweet child.
-Axel I.S. Icelandic

Cation Exchange: What it is, how it is measured, and does it matter?

Tom DeSutter

2021 Soil and Soil/Water Workshop

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