

A new CEC measurement proxy using high-frequency dielectric analysis of crushed rock

M. Rebecca Stokes¹, Z. Elton Yang¹, Prince Ezebuio¹, and Timothy Fischer¹

¹Chevron Energy Technology Company, Houston, Texas, USA

Abstract. Measuring the cation exchange capacity (CEC) of clay bearing rocks is a useful tool to estimate smectite content, or amount of swelling clay in the rock, and is referenced across many aspects of oil and gas exploration. Measuring the CEC of a rock, however, is laborious and depending on the method used requires saturation and extraction steps, the use of multiple chemicals, titration, and spectroscopic analysis. This study, which builds on the established petrophysical link between clays and relative permittivity (ϵ'), outlines a work flow and set of equations that allow for bulk rock CEC to be calculated from permittivity measurements of crushed rock using a handheld dielectric probe. A series of quartz-smectite mineral mixtures were prepared and high-frequency (80 MHz-1.4 GHz) dielectric measurements collected at six relative humidity (RH) conditions ranging from 8-75%. For each RH data set, a strong linear relationship ($R^2 \geq 0.98$) exists between permittivity at 120 MHz and the lab-measured CEC of the mineral mixtures. The equations from these calibration curves were used to derive 3 RH-dependent equations. The method was validated on a variety of crushed sedimentary rocks and differences between the calculated values from this study and the lab-measured CECs range between ± 6 meq/100g. These results demonstrate that dielectric permittivity measurements can be used as a CEC-proxy and is a fast and flexible alternative to laboratory-based CEC analysis.

1 Introduction

Cation exchange capacity (CEC) is a data type commonly referenced in the oil and gas industry as it holds critical information about the swelling potential of a rock which is an important component in well planning and production modeling. Specifically, quantification of clay types and their swelling behavior is used for drilling and completions planning, borehole instability mitigation, enhanced oil recovery (EOR) planning, and predicting changes in production due to damage from clay swelling. Each of these aspects of hydrocarbon production can be significantly impacted if the rocks of interest are not properly characterized with respect to the clays, and as a result there can be serious financial and Health and Environmental Safety (HES) consequences. The principal aim of this study was to develop a method to measure CEC quickly and without the use of chemicals or complicated analytical equipment so that CEC data can be available quickly to aid in decision making while drilling.

CEC is loosely related to the surface charge of a material and is the measure of the ability to reversibly adsorb cations. It is used across many geoscience and engineering fields to characterize clays. Exchangeable cations have varying hydration enthalpies due to the differences in their cation size and valence and as a result, the amount of water that can be adsorbed by a clay mineral

is dependent on the total specific surface area [1], and the exchangeable cation type located in the interlayer regions and particle surfaces. While most clay minerals have some CEC *e.g.* (kaolinite, chlorite < 5 meq/100g [2], illite $\approx 10-15$ meq/100g), smectite often has significantly

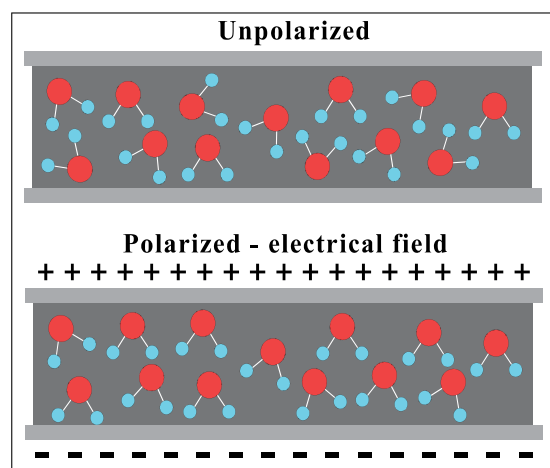


Figure 1. Schematic of water molecules with no electrical field versus an applied electrical field where the water molecules polarize.

greater CEC, sometimes an order of magnitude higher [3].

* Corresponding author: rebeccastokes@chevron.com

Thus, by measuring the CEC of a rock, one can estimate the approximate amount of smectite in the rock. Several methods exist to measure the CEC of a rock, and most involve the complete exchange of cations present in the natural sample by a cationic species, such as NH_4 , K^+ , Na^{2+} , methylene blue, $\text{Co(III)-hexamine}^{3+}$, and Cu(II) ethylenediamine complex [4]. Exchange is quantified by measuring the effluent solution by spectrophotometric techniques or by measuring the change in cation concentration in the fluid through mass spectroscopy. These methods, with some limitations (*e.g.*, [5, 6]) are effective CEC measurement methods, however they are time intensive, require the use of a chemicals which involve proper disposal, and a laboratory to store chemicals and house analytical equipment.

Relative permittivity (the real part of the complex permittivity) measures the degree to which a medium resists the flow of electric charge. Water is a polar molecule with a permanent dipole moment and will rotate to align with an applied electric field (Figure 1, [7]). We take advantage of this in the frequency region where the dielectric response of the rock is governed by dipole polarization ($\sim 10^8$ Hz). In this region, the effects of water, either in the form of adsorbed water on mineral surfaces, capillary water, or free water, makes permittivity measurements sensitive to CEC [8, 9], and thus to the amount of smectite present in the rock.

As CEC is an important mineral property to characterize in the oil and gas industry, several avenues of proxy CEC analysis have been developed, including the use of magnetic susceptibility [10] and dielectric permittivity. Specific to the use of dielectric analysis as a CEC tool, Garrouch (2018) provides a set of equations

information to solve for CEC and these data are often not readily available [9]. Leung and Steiger (1992) also published a standard test procedure for ultimately calculating the amount of hydratable clays in shales [11]. This method involves several steps including saturating the sample in a K^+ solution, centrifuging twice, washing the sample with rubbing alcohol, and taking the dielectric measurement. CEC is then calculated by a simple correlation between the dielectric constant and standard mixtures, similar to those used in this study. The authors [11] have developed a portable kit that includes all the equipment necessary to make the measurements. While both methods offer ways to calculate CEC from dielectric measurements, extra labor is still required to either attain additional data to calculate CEC (Garrouch method), or to prepare the sample for dielectric analysis (Leung and Steiger method). Considering this, there is room still to generate a simplified CEC-proxy using direct dielectric permittivity measurements.

Materials and Methods

2.1 Sample selection and characterization

Two sets of samples were prepared for this study: 1) quartz-smectite mixtures and 2) rock powders from a variety of sedimentary rock types. Rock samples were selected based on their bulk mineralogy as determined by X-ray diffraction (XRD) analysis and bulk CEC values to obtain a decent range of rock types and CEC values up to 45 meq/100g (Figure 2a). Porosity data was collected on 7 of the 9 rock samples from co-located plugs by Hg

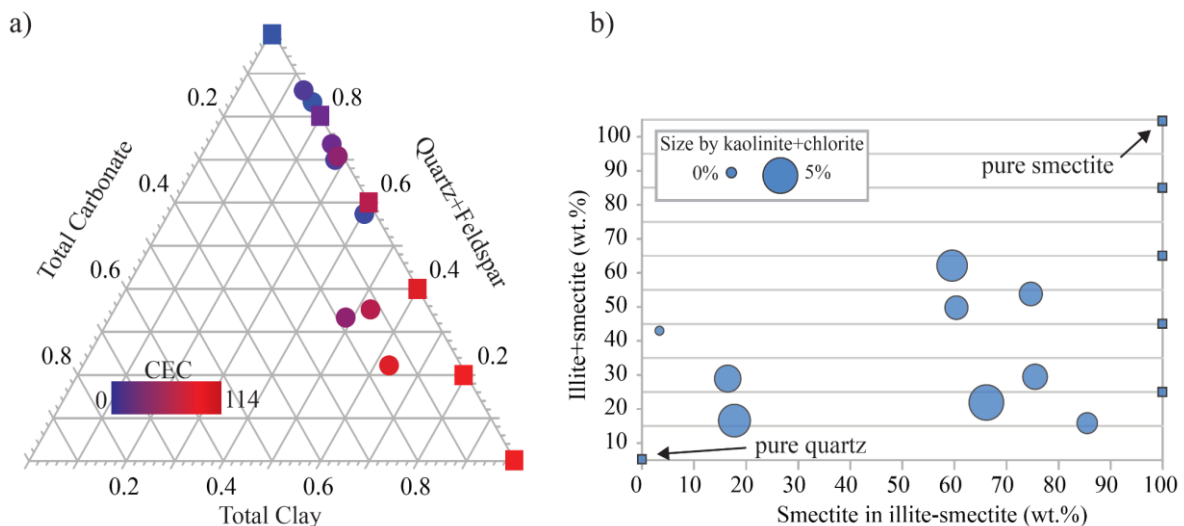


Figure 2. a) Summary of sample mineralogy on a ternary diagram including both quartz:smectite mixtures (squares) and rock powders (circles). Samples are colored by their CEC values from laboratory measurements. b) Illite-smectite wt.% vs. % smectite in illite-smectite (calculated using Equation (1)). Data points are sized by kaolinite+chlorite wt.%.

derived from dimensional analysis to calculate CEC, however these equations require surface area and porosity

porosimetry analysis on oven-dried and Dean Stark extracted material. Porosity values obtained using this

method range between 7-23%. Detailed information about the clay compositions and amounts as determined by XRD analysis are shown in (Figure 2b). Figure 2b shows illite-smectite wt.% plotted against the % smectite in illite-smectite (I-S) calculated using Equation (1). In this equation, %S in I-S is determined by assigning the bulk rock CEC to the total illite-smectite (CEC_{meas}) wt.% and normalized on a difference between pure illite end member ($CEC_I = 15$ meq/100g) and pure smectite end member ($CEC_S = 100$ meq/100g).

$$\%S \text{ in } I - S = \frac{CEC_{meas} - CEC_I}{CEC_S - CEC_I} \times 100 \quad (1)$$

Data points in Figure 2b are sized by kaolinite+ chlorite which does not exceed 5 wt.%. Both kaolinite and chlorite have a low CEC (<10 meq/100g) and are typically not considered significant contributors to bulk CEC.

The quartz-smectite standards were prepared by mechanically homogenizing 20% proportions by weight of pure quartz and a pure smectite (Tsukinuno montmorillonite JCSS-1301 distributed by The Clay Science Society of Japan) standard. Prior to homogenization the quartz was comminuted in a McCrone mill for 5 minutes so that the quartz particle size approximately matched that of the smectite standard. The rock powders were prepared by hand grinding the material in a mortar and pestle to pass through a 40 mesh (0.42 mm) sieve. This methodology for preparing the rock powders avoids common issues associated with artificially altering the CEC via sample preparation. Hand grinding minimizes shearing which might delaminate clay particles, and the particle size associated with a 40 mesh sieve is, for most rocks, larger than the average phyllosilicate grain size thus not increasing the surface



Figure 3. Handheld dielectric probe manufactured by Copper Mountain Technologies used in this study. The circular probe end (left side of probe) is ~1 inch in diameter.

area of the individual grains.

Both the quartz-smectite mixtures and rock powders were dried in an oven at 105°C for 48 hours to ensure that the majority of clay bound H₂O was removed [3]. Approximately 3 grams of material were loaded into a shallow plastic holder prior to being placed in the first relative humidity (RH) controlled desiccator. Samples were equilibrated for ~48 hours at each RH prior to dielectric analysis at each stage.

Splits were taken from all samples for CEC analysis and from the crushed rock samples for XRD analysis. These data are summarized in Figure 2a. CEC measurements were done using the Co(III)-hexamine³⁺ cation exchange, spectrophotometric technique outlined by Bardon et al. (1993) [12]. The rock powders were prepared for XRD analysis following the methods described in Środoń et al. (2001) and Omotoso et al. (2006) to make randomly oriented powder mounts [13, 14]. The phase quantification was accomplished using Chevron's proprietary software, which is a modification of a technique published by Chung (1974) [15].

Relative humidity was controlled by using a series of saturated salt solutions in desiccation chambers and monitored by a barometric pressure-temperature-relative humidity data logger located inside the chamber. In increasing order of RH, the salts used in this study included lithium chlorite (LiCl), lithium iodide (LiI), potassium acetate (CH₃CO₂K), magnesium chlorite (MgCl), potassium carbonate (K₂CO₃), sodium bromide (NaBr), and sodium chloride (NaCl). To achieve the RH between LiCl and LiI (RH=11.2%), equal amounts of two saturated salt solutions (LiCl and LiI) were placed in separate containers in a desiccator. In addition, an additional RH dataset was collected by leaving the samples to equilibrate in the room RH (58.8%) for 24 hours. Room RH was monitored during the equilibration

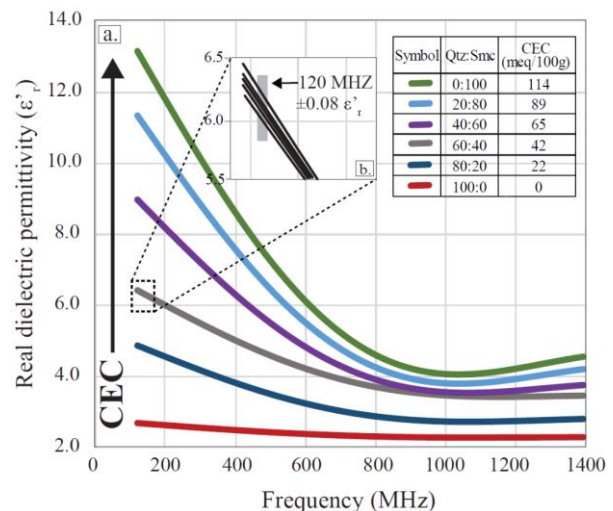


Figure 4. a) Real dielectric permittivity curves across the full frequency range for the 6 quartz-smectite used in this study. b) Example of the typical range observed at low frequencies between the 5 repeated dielectric analyses. Errors based on this are reported in Figure 5.

and did not deviate more than ±1.5%.

Water vapor adsorption analysis using the Dynamic Vapor Adsorption (DVS) machine developed by Surface Measurement Systems Ltd. was used to quantify the amount of water adsorbed by smectite at the specific RH conditions investigated in this study. This specific machine uses a gravimetric sorption technique that measures how quickly and how much of a solvent is adsorbed by a sample.

2.2 Dielectric measurement method

The Dielectric Assessment Kit System (Schmid & Partner Engineering AG, Switzerland) with a Planar R140 Vector Reflectometer (Copper Mountain Technologies vector network analyzer) and a DAK-3.5 probe was used to perform the laboratory dielectric measurements on each of the powder samples (Figure 3). The Vector Network Analyzer (VNA) operates from 85 MHz to 1.4 GHz, and the Depth of Investigation (DOI) of the DAK-3.5 probe is ~3 mm.

The dielectric probe was always calibrated at room temperature (~21°C) before usage. During the measurement at each designated RH, the probe remained vertical with the active surface area directly touching the top of the sample. A small amount of pressure was used to minimize the gap between the probe and the sample. After the permittivity readings stabilized, the values within the entire sweeping range (5 MHz resolution) were recorded (Figure 4a). The same measurement was repeated five times on each sample to ensure the reliability of the measurement and the average of those readings was used in the study. The typical observed ϵ'_r range from 5 repeat measurements at 120 MHz is ± 0.08 (Figure 4b).

Figure 4a shows the influence of CEC on the dielectric response across the full range of frequencies. The largest difference between these curves is at the lower frequencies, thus we chose to read the real dielectric permittivity at 120 MHz for this study.

It should be noted that the laboratory RH was typically ~55%, consequently collecting the data for the lower RH conditions had to be done quickly. If a sample was exposed to the room RH conditions for more than 1 minute, it was placed back in the desiccator to re-equilibrate to the low RH condition and then analyzed again. As a result, the datasets for the RH conditions <30% took many days to collect.

3 Results

3.1 Dielectric Results

3.1.1 Quartz-smectite mixtures

Dielectric measurements of the quartz-smectite mixtures were collected to characterize and quantify the relationship between CEC, permittivity, and relative humidity. These results are shown in Figure 5. Each RH dataset shows a very strong correlation between permittivity and CEC with R^2 values >0.98. The pure quartz sample (CEC=0) has a relatively constant permittivity value of ~2.5 despite the large range of RH conditions. At this point in the study, had the slope (and y-intercept) differences between each dataset showed a linear relationship with RH, a CEC calculation would be straightforward using a line equation and a multiplication

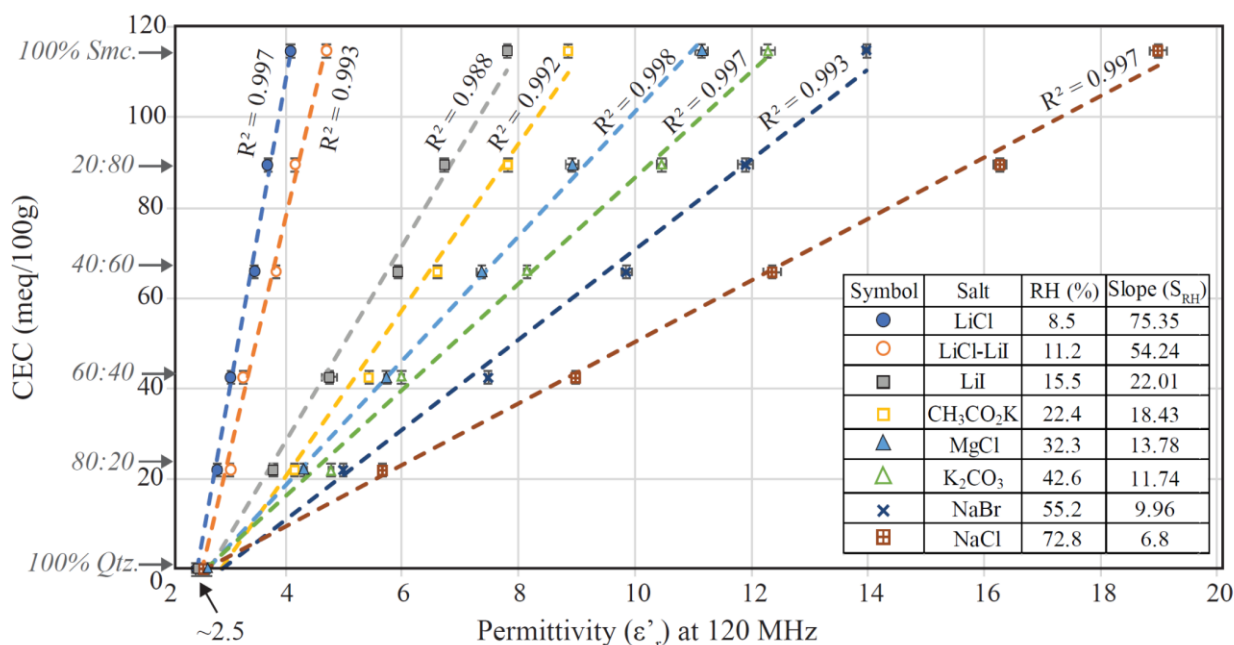


Figure 5. Dielectric permittivity at 120MHz results from the 6 quartz-smectite mixtures at 8 different RH conditions. All data was collected at 21°C. Dashed lines and corresponding R^2 values are the best fit line for each dataset. CEC error from laboratory measurements is ± 1.8 meq/100g and permittivity errors are from the range of values for the 5 repeat dielectric analyses collected on every sample at each RH. Quartz:smectite ratios are noted in grey italicized lettering on the left side of the plot.

factor for the slope-RH relationship. However, these datasets yield a non-linear relationship between the slope (S_{RH}), y-intercept constant (c_{RH}), and relative humidity which needs to be further constrained to successfully calculate CEC using Equation (2).

$$CEC = S_{RH} \varepsilon_r' + c_{RH} \quad (2)$$

The slope values (CEC / ε_r') shown in Figure 5 are plotted against their corresponding RH value in Figure 6 to establish the relationship between CEC and permittivity as a function of RH from 8% to 72% at 21°C. It becomes apparent that there are three linearly-related regions defined by the intersection of best fit lines at low (<18%), moderate (18-35%), and high (>35%) RH conditions. The best fit lines for these regions have R^2 values >0.98. It should be noted that a single curve approach to fitting the data was evaluated, however, due to the sharp change in slope between the mid and high RH regions, simple exponential and power decay equations were not adequate to fit the full dataset. It should also be addressed that the mid-range RH best fit line is defined by only two data points, and we recognize that more data points would make a stronger case for the following interpretations. Despite the limited number of data points, errors ($CEC_{measured} - CEC_{calculated}$) of calculated CEC values reviewed in Section 3.2.1 and are reasonable, suggesting that the addition of more data points would not change the correlations.

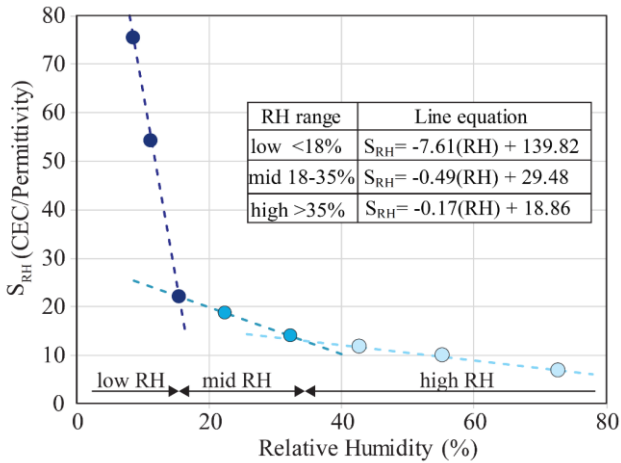


Figure 6. Relationship between the slopes derived from Figure 5 and relative humidity.

The three, RH dependent, linear curves (Figure 6) provide equations that allow for S_{RH} to be calculated using Equation (3).

$$S_{RH} = S_{l,m,h}(RH) + c_{l,m,h} \quad (3)$$

The parameters required to solve for S_{RH} are $S_{l,m,h}$ and $c_{l,m,h}$ which are the slope and y-intercept values provided in the table embedded in Figure 6; l , m , and h stand for low-, mid-, and high-RH conditions. Their respective values should be substituted into Equation (3) depending on the RH recorded during permittivity data collection. Now that

S_{RH} can be calculated, c_{RH} can be calculated using Equation (2). This is possible because the best-fit lines for each RH meet at $2.5 \varepsilon_r'$, $CEC=0$ (see Figure 5) thus leaving a simple equation to solve for c_{RH} (Equation 4).

$$c_{RH} = -S_{RH}(2.5) \quad (4)$$

3.1.2 Crushed rock samples

Dielectric analysis results on the crushed rock samples at 32.3% and 72.8% RH are plotted in Figure 7. These data are shown together with the lower CEC quartz-smectite mixture data from the same RH conditions where the dashed lines are the same as the best-fit lines shown in Figure 5. There is good agreement between the crushed rock data and quartz-smectite mixtures despite significant differences in particle size, porosity, and mineralogy - specifically clay speciation (Figure 2a, b).

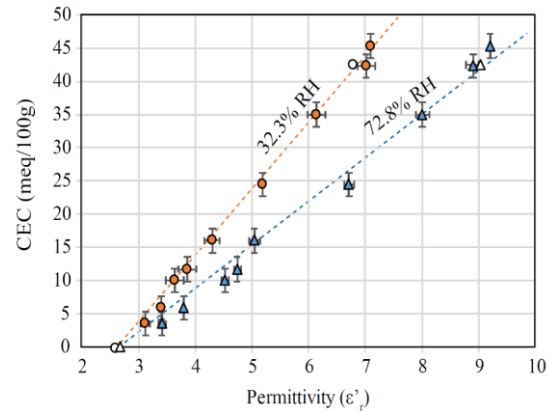


Figure 7. Permittivity vs. measured CEC for the crushed rock samples (filled shapes) at 32.3% and 72.8% RH. Dashed lines are the best-fit lines defined by the quartz-smectite mixtures (open shapes) shown in Figure 5.

3.2 Water-Vapor Adsorption Results

Water vapor adsorption results provide information about the amounts of adsorbed water and rate of adsorption that ultimately control the permittivity. In this paper we do not show the rate of water adsorption data from these experiments, however this component of the data provided valuable information regarding how quickly high CEC samples adsorb H_2O , thus altering the way we collected data and treated samples prior to, and during dielectric analysis. Figure 8 shows the relationship between permittivity and the amount of adsorbed H_2O by smectite as a function of RH. At low RH conditions, the steep slope of the best-fit line establishes that the addition of relatively small amounts of water vapor to dry smectite has a very strong impact on the dielectric response of the material. This strong dielectric response lessens by an order of magnitude around 18% RH which, unsurprisingly, corresponds to the boundary between the low- and mid- RH regions identified in Figure 6.

$$CEC = S_{RH} \epsilon'_r + c_{RH} + C \quad (5)$$

Adjusted calculated CEC values using Equation 5 are plotted against laboratory measured CEC in Figure 9. There is good agreement within ± 6 meq/100g between calculated and measured CEC for all samples (quartz-smectite and crushed rock samples) from 8-73% RH.

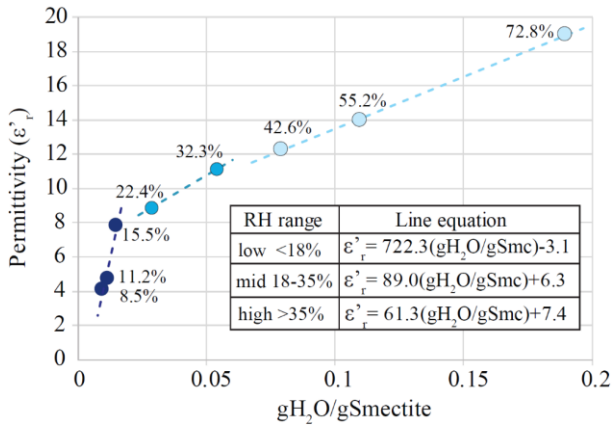


Figure 8. Permittivity vs. amount of water adsorbed by pure smectite at specific RH conditions (% next to circles) that match those investigated in this study.

3.3 Method Validation

Using Equations (2)-(4), CEC was calculated for the quartz-smectite and crushed rock samples to evaluate the method presented in this paper. There was a consistent positive offset of the calculated CEC from the lab-measured CEC of ~ 4 meq/100g. This correction factor (C) is applied to Equation (2), yielding Equation (5). The

4 Discussion

4.1 Method application and limitations

This study was motivated by the need for a portable CEC analysis technique that does not require significant sample preparation or the use of chemicals. Creating a method to quickly generate CEC data would be particularly useful for drilling engineers and geologists to assess changes in the swelling potential of rocks being drilled and account for potentially impacted processes in real-time. The method presented in this paper provides a procedure and set of equations for a CEC-proxy tool that can be developed for specific laboratory/field conditions where RH (and temperature) conditions are often not constant.

Identified limitations of this technique include: 1) Specific values provided for $S_{l,m,h}$, $c_{l,m,h}$, and C are only applicable if collecting data at the same temperature (around 21°C in this study) and frequency (120 MHz). Permittivity measurements in the high-frequency range

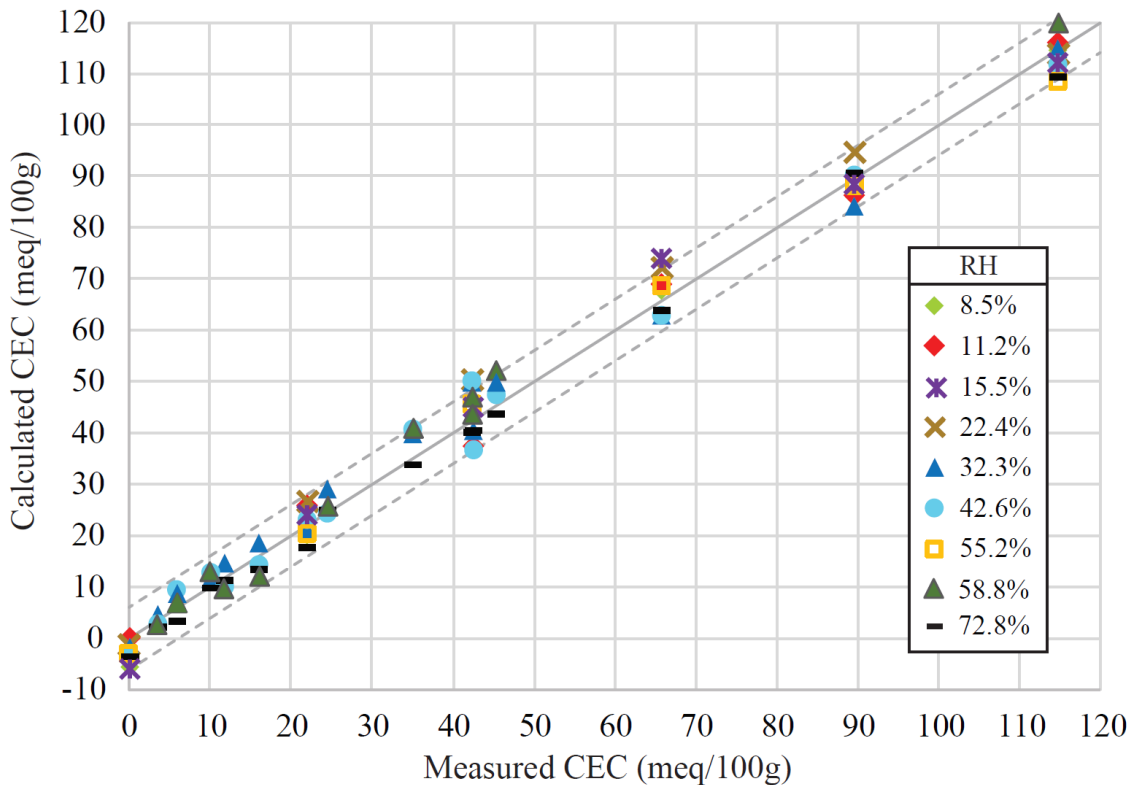


Figure 9. Calculated CEC using Equation 5 vs. the laboratory measured CEC for the crushed rock samples (max. CEC of 45 meq/100g) and quartz:smectite standards. Solid grey line is the 1:1 line, dashed grey lines define the ± 6 meq/100g error field.

source of this error is worth investigation though it is not evaluated in this paper.

are sensitive to changes in temperature [16], thus operating conditions outside of this will require new calibration curves similar to what are shown in Figure 5

such that new values can be calculated for $S_{l,m,h}$, $C_{l,m,h}$, and C . However, once established, the analyses and CEC calculations are straight forward and fast to obtain. 2) This study attempted to use a wide range of rock types to validate the method (Figure 2) however, there are some minerals/phases that were not covered and may not be suitable for this method. These include Mg-dominant smectite, certain zeolites, opal varieties, significant amounts of solid organic matter [5], and grain coating liquid hydrocarbon. Other parameters that showed surprisingly little to no impact on the dielectric response were porosity, particle size, and compositional variations of illite-smectite (*e.g.* exchangeable cations and associated variations in layer charge). 3) This method has been validated for use in RH conditions ranging from 8-73% RH. At very low RH condition, there will not be enough H₂O in the system to be conducive to dielectric analysis. At very high RH conditions (>~75%) it is well documented that capillary condensation in porous media dominates water sorption mechanisms and is a phenomenon mostly independent of CEC (*e.g.* [16]). Both scenarios would significantly complicate the relationship between RH, CEC, and permittivity.

4.2 Clay-water interaction and dielectric response

An outcome of this study that requires further investigation are the physiochemical processes governing the relationship between S_{RH} and RH as shown in Figure 6. At RH conditions below ~18%, there is a strong dielectric response to very little H₂O in the environment and above this the response is not as strong relative to the ever-increasing amounts of H₂O adsorbed by smectite. In the case of pure smectite, the water adsorption behavior in this RH region is largely controlled by the size and valance of the exchangeable cation in the TOT (tetrahedral-octahedral-tetrahedral) interlayers and their corresponding hydration enthalpies ($Mg^{2+} \gg Ca^{2+} > Na^+ > K^+$) [18]. Numerous studies have used X-ray diffraction to describe smectite swelling behavior through tracking the changes in the basal d-spacing of different smectite species at a range of RH conditions [19-22]. These results consistently show that interlayer expansion for K⁺, Na⁺, Ca²⁺, and Mg²⁺-exchanged smectite typically starts at >20%, ~20% RH, ~20% RH, ~10%RH, and <10%RH, respectively. The smectite (Tsukinuno montmorillonite) used in this study is Na²⁺-dominant (>75%) with measurable amounts of Ca²⁺ and Mg²⁺ (Ca>Mg) [23]. Based on this information, most of the interlayer expansion via H₂O adsorption starts around 20% RH which corresponds to the drastic change in the S_{RH} -RH relationship identified in this study at 18% RH. It follows that at RH conditions lower than ~20%, the large changes in permittivity are possibly due to H₂O adsorption on high CEC mineral surfaces and edges, however this theory needs further investigation. As RH increases and smectite interlayer adsorption begins to dominate, the dielectric response decreases relative to the increased adsorption of interlayer H₂O.

At higher RH values, a more subtle change in the relationship between S_{RH} and RH occurs at ~35% RH, and

defines the boundary between the mid- to high- RH ranges shown in Figure 6. This RH value corresponds to published data that mark the prevalence of monolayer adsorption of H₂O around cation/charged sites in Namontmorillonite similar to the smectite standard used in this study [17, 19, 25]. This loose interpretation of the data from this study requires further evaluation, however if a physiochemical-based explanation for the empirical relationships identified between RH, CEC and dielectric response can be provided, it would make an even stronger case for the use of dielectric permittivity as a proxy for CEC.

5 Conclusions

Results of this study provide a set of equations and methodology that allow CEC to be calculated from the real part of the complex permittivity. To do this, a series of equations were developed to determine the RH dependent relationship between CEC and permittivity such that if the RH is known and the permittivity measured, bulk CEC can be calculated. Approximate error for the CEC calculation using these equations is ±6 meq/100g which for the purposes of discriminating rocks that will have issues due to clay swelling, is acceptable.

The handheld tool used for dielectric analyses is portable and relatively easy to set up and calibrate. Sample preparation only requires hand grinding the rock to pass through a 40-mesh sieve and oven drying the sample to remove any water and liquid hydrocarbons, if present, and equilibrating the sample to a single RH for at least 24 hours. This tool and set of equations are a portable and easy to use option for calculating CEC *in lieu* of traditional laboratory-based methods.

Future areas of investigation related to this study include: 1) investigate CEC-RH relationships at various frequencies and for various exchangeable cations 2) applying the learnings from this study to assess obtaining CEC data from dielectric log data, 3) the fundamental molecule-surface interactions contributing to dielectric permittivity in mineral mixtures and, 4) using this tool for CEC analysis on slabbed core.

Acknowledgements

We would like to thank Chevron Energy Technology Company for funding this research and providing the analytical equipment and materials. We would also like to acknowledge and thank Hanming Wang, Boquin Sun, Russ Peacher, Jon Burger, and Douglas McCarty for their technical contributions and guidance on this project.

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