[PS]Experimental Measure of Clay Cation Exchange Capacity and Modeling of Factors Critical to Reservoir Desiccation*

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Abstract

This study focuses on the controls of extensive sediment dewatering (desiccation), and presents a quick and inexpensive method by which cation exchange capacity (CEC) may be measured in mudrocks. Statistical models for organic maturation, and CEC are generated for high resolution characterization of desiccation in argillaceous intervals. CEC models were calibrated against XRD/SEM measurement-based calculations of clay CEC expected under modeled in-situ conditions. CEC measurements were completed via wet chemistry (cobalt hexamine trichloride) and inductively coupled mass spectrometry. The effects of sample grinding are corrected for via differential sample grinding times as described by Huff 1987. Clay CEC and organic content are major factors in the response of a reservoir to injected fluids, a critical relationship for unconventional well decline curve analyses. Understanding the mechanisms controlling fluid expulsion and imbibition in unconventional tight reservoirs is a critical economic issue. Our current hypothesis is that measured clay CEC will be significantly less than calculated values, due to the surface area dependent nature of cation exchange. CEC calculations often ignore grain size and morphology, resulting in models that do not respect real-world grain geometries, and pore-fluid interactions which may shift exchange values. Consequently, we also hypothesize that water saturation is proportional to CEC in tight rocks. Higher clay CEC values being associated with elevated water saturations. Unpublished preliminary statistical work has suggested that although the proposed relationship may not be 1:1, correlation is strong. Finally, we hypothesize that clay CEC, porosity, and organic maturity are the greatest influences on the effectiveness of natural reservoir desiccation.

References Cited

Derkowski, A, and T. Bristow, 2012, On the Problems of Total Specific Surface Area and Cation Exchange Capacity Measurements in Organic-Rich Sedimentary Rocks: Clays and Clay Minerals, v. 60, p. 348-362. doi.org/10.1346/CCMN.2012.0600402

Engelder, T., L. Cathles, and L.T. Bryndzia, 2014. The Fate of Residual Treatment Water in Gas Shale: Journal of Unconventional Oil and Gas Resources, v. 1, p. 33-48.

Hubbert, M.K., and W.W. Rubey, 1959, Role of Fluid Pressure in Mechanics of Overthrust Faulting: 1 Mechanics of Fluid Filled Porous Solids and Its Application to Overthrust Faulting: Geological Society of America Bulletin, v.70, p.115-166. doi.org/10.1130/0016-7606(1959)70[115:ROFPIM]2.0.CO;2

Huff, G.F., 1987, A Correction for the Effect of Comminution on the Cation Exchange Capacity of Clay-Poor Sandstones: SPE Formation Evaluation v. 2/3, SPE-14877-PA, 7 p. doi:10.2118/14877-PA

Martin, P., and J. Dacy, 2004, Effective Qv By Nmr Core Tests: Society of Petrophysicists and Well-Log Analysts, SPWLA 45th Annual Logging Symposium, 6-9 June, Noordwijk, Netherlands, SPWLA-2004-HH, 14 p.

Saidian, M., J.L. Godinez, and M. Prasad, 2016, Effect of Clay and Organic Matter on Nitrogen Absorption Specific Surface Area and Cation Exchange Capacity in Shales (Mudrocks): Journal of Natural Gas Science and Engineering, v. 33, p. 1095-1106. doi.org/10.1016/j.jngse.2016.05.064

Zhang, J, 2011, Pore Pressure Prediction from Well Logs: Methods, Modifications, and New Approaches: Earth-Science Reviews, v. 108, p. 50-63. doi.org/10.1016/j.earscirev.2011.06.001

Experimental Measure of Clay Cation Exchange Capacity and Modeling of Factors Critical to Reservoir Desiccation

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Headlines & Importance:
- Cation exchange capacity (CEC) important for reservoir characterization.

- Great need for time-efficient and accurate measured CEC methods in lab-based core studies.

- Desiccation critical for EOR method of soaking.

Introduction & Objectives
- CEC is the ability of a material to exchange ions with the surrounding fluid.
  - Is a function of material surface charge, surface area, temperature, salinity, and PH.
- CEC important for formation fluid saturations, wettability, and development strategies for unconventional reservoirs.
- Numerous reported methods for inferring of CEC from CEC sensitive logs or calculations from average values.
- We use the measured CEC method described in Huff, 1987 for clay-poor sandstones as a starting point, making alterations as required for CEC measurement in clay-rich mudstones.
- Many issues in subsurface geoscience have been addressed by soil characterization efforts; this study adds value to subsurface geology by bridging the gap between these two areas of study.

Background
- Reservoir desiccation index: ratio of capillary-bound-water to clay-bound-water.
- Theory process: hydrocarbons (HC) enter the pore space increasing pressure, forcing water to dissolve into the HCs. The water saturated HCs are then cyclically expelled from the pore system. This process repeats itself until all capillary-bound-water has been expelled and then again for all clay -bound -water, Engelder et al (2014).
- Soaking enhanced oil recovery, post-fracking procedure where fracking fluids are permitted to soak for an extended period. Associated with increased fracture half-length, extended elevation of HC production, and decreased water production.

Comparison of Desiccation Index to Basic Formation Properties

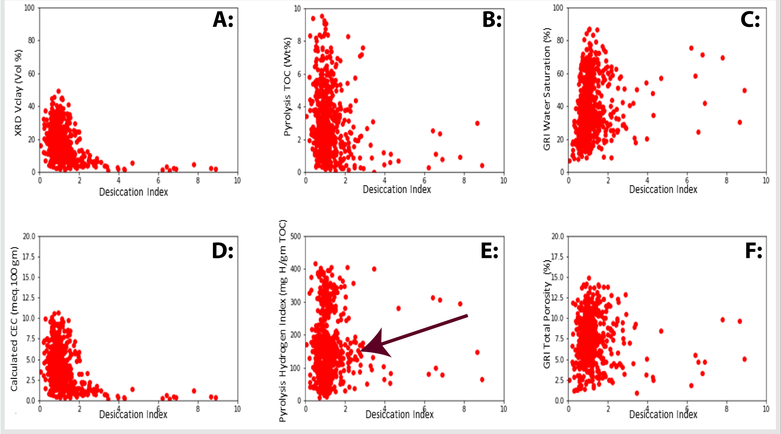


*Figure 1: Desiccation index (x-axis) vs: **A:** X-Ray diffraction derived clay volume percent, **B:** Total weight percent organic carbon, **C:** Gas Research Institute (GRI) Crushed shale derived water saturation, **D:** Martin and Dacy,2004 XRD calculated CEC, **E:** Pyrolysis hydrogen index, and GRI total porosity. Arrows indicate aproximate trajectory of points with changing y-axis values. **A:** Larger clay volumes tend to be associated with lower desiccation index values. **B:** Large values of total organic carbon tend to be associated with lower desiccation index values. **C:** Water saturation generates a cone-like distrobution when compared to desiccation index, lowest desiccation index value for a given water saturation bounded by sharp discontinuity. **D:** Desiccation values decrease with increasing calculated CEC. **E:** Pyrolysis hydrogen index provides an indication of organic maturity, as organic maturity increases, we infer that points on this plot will migrate to the x-y axis intercept. **F:** Total GRI derived porosity generates a cone shaped scatter similar to the GRI derived water saturation.*

Correlation and Covariance of Desiccation Properties vs XRF Measured Elements

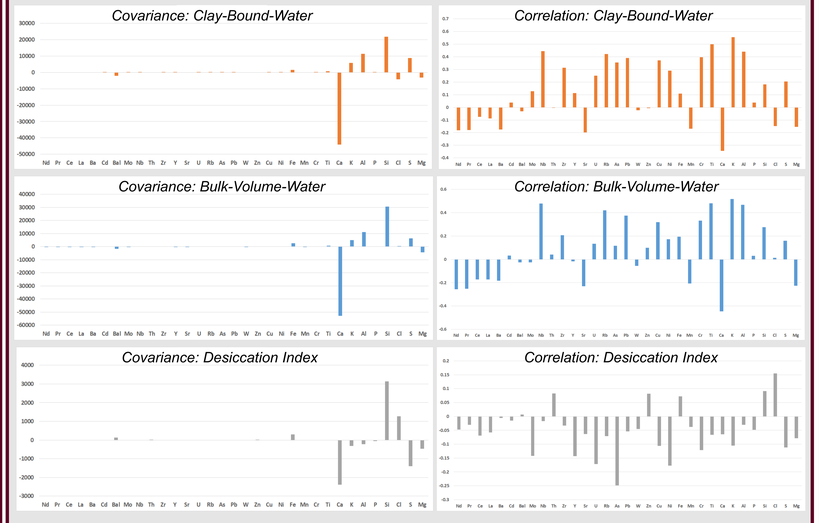


*Figure 2: Correlation and covariance of clay bound water, bulk volume water, and desiccation index vs XRF measured elemental concentraion. **Left column:** covariance, **right column:** correlation, **top to bottom:** clay-bound-water, bulk-volume-water, desiccation index. Covariance of iron, calcium, potassium, aluminum, silicon, chlorine, sulfur and magnesium most prominant vs desiccation properties. Correlation of Arsenic, nickel, iron, titanium, phosphorus, chlorine, and sulfur most prominent when compared to desiccation and desiccation properties. Null values have been removed.*

Results & Discussion

CEC of individual clay species is not as critical as the weight or volume of that species present in the rock. For example, although smectite has the highest average CEC of all clay minerals, if there is more illite in a rock, illite will have the larger contribution to whole rock CEC.

Although numerous factors have discernable influence over final reservoir desiccation values, total porosity, total clay and organic content show coherent trends when compared to desiccation (Figure 1). Total porosity and water saturation show a positive relationship, whereas clay volume shows an inverse relation to desiccation values. Measured water saturation is the end result of desiccation; although initial water saturation is important it will be altered by diagenetic processes.

Larger values of weight percent TOC are associated with lower desiccation index values (Figure 1). A similar trend is observed with measured vitrinite reflectance, greater values associated with lower desiccation index. (Figure 1). This gives further credence to the theory of sub irreducible water expulsion by hydrocarbon generation.

Redox elements Mo, As, Ni, and U have strong negative correlation with desiccated points; redox elements at greater concentration where desiccation index is small (Figure 2). Thus suggests association of organic content and desiccation, which is congruent with the Engelder et al (2014) model. Likewise concentrations of Ca, K, Al, Si, S, and Mg have strong negative covariance vs desiccation index relative to all other 41 measured elements. (Figure 2). These elements, in exception of Si, are commonly used as target elements in measured clay CEC experiments. Results suggest the presence and abundance of clay species and their mixing effects measured cation abundance. Strong positive covariance of silicon to desiccation index may be attributed to positive relationship between clay and clay-bound-water. We conclude that there is statistical credence to the desiccation model proposed by Engelder et al (2014). Selection of redox elements by stepwise CEC determination suggest organic-clay interactions may be common and play a role in desiccation (Figure 1, Figure 4).

Combination of Cobalt(III)Hexamine, and ICP-MS permits rapid and cost effective means for generating logs of measured CEC across cored intervals or outcrops. Due to small sample size required for analysis and correction, this procedure may be added to existing core analysis workflows without significant additional sample loss. This permits denser sample spacing across cores and outcrops, capturing finer scale changes in rock properties critical to wettability and saturation.

Pressure-facies inferred from the sonic log correspond well with breaks in log and lab derived porosity trends (figure 3). Sonic predicted pore pressures show positive correlation with bulk volume water and GRI determined water saturation, showing a planar distribution in 3D space that dips away from high bulk volume water values (Figure 3). This suggests water associated overpressure at the given location. In conclusion, the success of soaking enhanced oil recovery may be a balance between lithological properties critical to desiccation (e.g. clay content, porosity), diagenetic and burial history, and interaction between injected fluids and the formation/formation fluid.

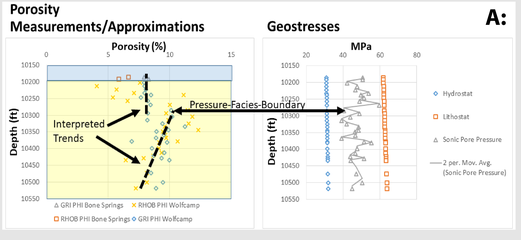
Data and Methods
Project data is a combination of clay mineral standard samples procured from the Clay Mineral Society, and XRF, XRD, GRI, organic and organic maturity data, and log data provided by collaborators.

XRF CEC Extrapolation: Correlation and covariance of various elements are analyzed against XRF measurments. This dat is then used to generate linear regression models for CEC extrapolation.

Evaluation of Geo-Stresses: Pore pressures are predicted in select wells within the study area for the investigation of relationship between geostresses and desiccation. Pore pressures are predicted from sonic logs following Bowers' method as described in Zhang, 2011, and validated via GRI measured porosity values.

Measure and correction of CEC:
1. Standard samples are ground, mixed in various end-member combinations, and analyzed via XRD and XRF for determination of exact mineralogical composition and elemental concentrations.
2. Mixed samples are then individually split into four sub-samples which further ground for differing lengths of time.
3. 1 gram of each sample is mixed with 25ml of Co(III)-hexamine, and centrifuged at 5000 rpm for 10 min as described in Derkowski and Bristow, 2012.
4. Fluid from sample-Co(III)-hexamine solution was then siphoned off and measured via inductively coupled plasma mass spectrometry (ICP-MS) for measurement of un-adsorbed Co(III)-hexamine.
5. Data from step four was then used to determine the mass of adsorbed Co(III)-hexamine, which was used to calculate the CEC of clay within the sample.
6. Multiple CEC measures at differing degrees of sample grinding are correlated for correction to in-situ conditions following Huff, 1987.

Evaluation of Geo-Stresses



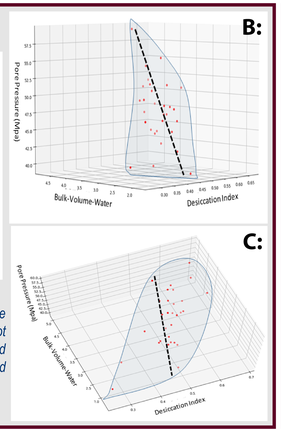


*Figure 3: **A:** comparison of log and lab derived porosities against sonic log inferred pore pressures. Pressure facies inferred on basis of sonic log and trends in porosities. **B and C:** 3D plot of sonic inferred pore pressures against bulk-volume-water and desiccation index. The blue shaded region outlines the interpreted surface, the dashed black line indicates the dip of the interpreted surface. **B:** Looking into the interpreted plane **C:** Looking down on the interpreted plane.*

XRF CEC Extrapolation

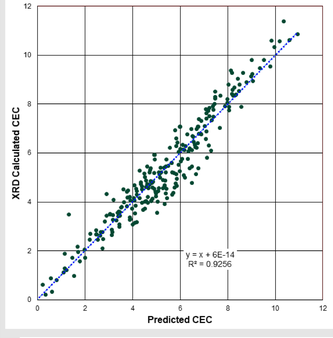


*Figure 4: **Top:** XRD calculated CEC following Martin and Dacy, 2004 vs regression predicted CEC, blue line and equation show fit of data. **Bottom:** variables selected for regression equation. Elements are XRF measured concentrations, clay weight percent is determined via XRD. Variables are selected via stepwise methodology based on correlation and covariance of variable to calculated CEC.*

$$CEC_{Regression} = f(As, Ni, Fe, Ti, P, Cl, S, Clay\ (wt\%))$$

References
Derkowski, A. and Bristow, T, 2012, On the Problems of Total Specific Surface Area and Cation Exchange Capacity Measurments in Organic-Rich Sedimentary Rocks: Clays and Clay Minerals, V. 60, p. 348-362, doi.org/10.1346/CCMN.2012.0600402

Saidian, M., Godinez J. L, and Prasad, M, 2016, Effect of clay and organic matter on nitrogen absorption specific surface area and cation exchange capacity in shales (mudrocks), v. 33, p. 1095-1106, doi.org/10.1016/j.jngse.2016.05.064

Zhang, J, 2011, Pore Pressure prediction from well logs: Methods, Modifications, and new approaches: Earth-Science Reviews, v. 108, p. 50-63, doi.org/10.1016/j.earscirev.2011.06.001

Hubbert, M, K, and Rubey, W.W, 1959, Role of Fluid Pressure In Mechanics of Overthrust Faulting: 1 Mechanics of FLuid Filled Porous Solids and Its application To Overthrust Faulting: GSA Bulletin, v.70, p.115-166, doi.org/10.1130/0016-7606(1959)70[115:ROFPIM]2.0.CO;2

Martin, P., and Dacy, J., 2004, Effective Qv By Nmr Core Tests. Society of Petrophysicists and Well-Log Analysts.

Huff, G. F., 1987, A Correction for the Effect of Comminution on the Cation Exchange Capacity of Clay-Poor Sandstones: SPE Formation Evaluation, doi:10.2118/14877-PA