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Research paper

A new method for quantifying cation exchange capacity in clay minerals

Kai Cheng^a, Zoya Heidari^{b,*}^a Department of Petroleum Engineering, Texas A&M University, College Station, TX, USA^b Petroleum and Geosystems Engineering, The University of Texas at Austin, TX, USA

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ABSTRACT

In this paper, a new method is proposed to theoretically quantify cation exchange capacity (CEC) of pure clay minerals, by use of nuclear magnetic resonance (NMR), X-ray diffraction (XRD), and nitrogen adsorption-desorption isotherm analysis. A theoretical model is introduced to estimate CEC, which is derived based on energy balance between chemical potential and electric potential energy. The change in chemical potential is a function of relative humidity and volume of hydration water. The change in electric potential energy is a function of the CEC, basal spacing, and surface area of clay minerals. XRD measurements were performed on clay minerals before and after exposure to 95% relative humidity. These measurements were used to estimate the basal spacing before and after hydration as well as the number of interlayers in each particle of clay minerals. NMR laboratory measurements were performed on the clay mineral samples before and after hydration to obtain the volume of hydration water. The nitrogen adsorption-desorption isotherms provided the surface area of clay minerals. The estimates of CEC from the new method were cross-validated against the directly-measured CEC, obtained from ammonium acetate method by use of inductively coupled plasma mass spectrometry (ICP-MS) measurements. The introduced method was successfully tested on six types of clay minerals (i.e., illite, kaolinite, chlorite, and three types of montmorillonite). The calculated CEC results from the new method were in agreement with those from the wet chemistry method, with less than 7 meq/100 g difference for all types of clay minerals. The experimental results on the performance of the new method demonstrated reliability of this method for quantification of CEC. The outcomes of this paper can be potentially applied to variety of formations with measurable concentrations of clay minerals such as shaly sands and organic-rich mudrocks for reliable assessment of CEC.

1. Introduction

The clay minerals, which carry large number of exchangeable cations, are abundant in hydrocarbon-bearing formations, such as shaly sands and organic-rich mudrocks. The quantity of these positive exchangeable ions per unit mass of dry rock is defined as cation exchange capacity (CEC) (Johnson and Linke, 1978; Bergaya and Lagaly, 2006; Bergaya et al., 2013). The presence of the exchangeable cations in clay minerals significantly affects quantitative interpretation of electrical resistivity for assessment of hydrocarbon saturation. For instance, shaly-sand resistivity models such as (Waxman and Smits, 1968), take CEC per unit pore volume of the rock, as an input to compensate the influence of clays on electrical resistivity measurements. Therefore, reliable assessment of CEC is crucial for dependable interpretation of electrical resistivity logs, assessment of hydrocarbon reserves, and production operations in clay-rich formations.

Methods such as wet chemistry, multiple salinity, and membrane potential are typically used for CEC quantification. There are, however,

limitations associated with each one of these methods. Wet chemistry method uses ammonium or barium ions to extract the exchangeable cations from clay minerals and estimates CEC based on concentration of extracted cations (Chapman, 1965). CEC estimated using this method varies with particle size of clay minerals and pH of solution (Pinnavaia, 1983). Multiple salinity method for CEC estimation is based on resistivity measurements on the intact core plugs, which are saturated with brine at different salinity (Mian and Hilchie, 1981). This method is, however, only applicable for high permeability formations, which allow brine flow through the rock (Martin and Dacy, 2004). Membrane potential method (Thomas, 1976) requires an apparatus that could use drill cuttings as membranes in an electrochemical cell and measure the voltage using Ag-AgCl electrodes for calculating CEC. This method relies on empirical correlations between CEC and the measured voltage, obtained from previous measurements in any given shaly sand formation of interest. Such correlations are highly sensitive to the types of clay minerals in the formation and not necessarily reliable in other formations. All of the aforementioned existing methods for CEC

* Corresponding author.

E-mail address: zoya@utexas.edu (Z. Heidari).

Nomenclature

CEC Cation exchange capacity of clay minerals (meq/100 g)
CEC_{Ca2+} CEC of Ca²⁺ in clay minerals (meq/100 g)
CEC_{K+} CEC of K⁺ in clay minerals (meq/100 g)
CEC_{Mg2+} CEC of Mg²⁺ in clay minerals (meq/100 g)
CEC_{Na+} CEC of Na⁺ in clay minerals (meq/100 g)
d Basal spacing before swelling (Å)
d' Distance between two successive layers before swelling
d_{1/2} Distance from cations to the surface of clay minerals before hydration (Å)
D Basal spacing after swelling (Å)
D' Distance between two successive layers after swelling
D_s Thickness of hydration water on the surface of clay minerals (Å)
D_{1/2} Distance from cations to the surface of clay minerals after hydration (Å)
e Elementary charge (1.6022 × 10⁻¹⁹C)
E Electric field strength (V·m⁻¹)
ΔG Gibbs free energy change of the hydration reaction (J·mol⁻¹)
ΔG⁰ Standard-state Gibbs free energy change of the hydration reaction (J·mol⁻¹)
i Type of cation (i.e., Na⁺, Mg²⁺, K⁺, or Ca²⁺)
K Dimensionless shape factor
K_p Equilibrium constant of hydration reaction
Mass_{clay} Total mass of clay minerals (g)
m_{Ca2+} Atomic mass of Ca²⁺ (40.1 g·mol⁻¹)
m_{K+} Atomic mass of K⁺ (39.1 g·mol⁻¹)
m_{Mg2+} Atomic mass of Mg²⁺ (24.3 g·mol⁻¹)
m_{Na+} Atomic mass of Na⁺ (23.0 g·mol⁻¹)
m_w Water molar mass (18.0 g·mol⁻¹)
n The order of reflection in Bragg's law
N Average number of interlayers
N_A Avogadro constant (6.0221 × 10²³ mol⁻¹)
N_{c,i} Quantity of cation *i*
P_{clay(s)} Partial pressure of dry clay minerals (atm, 1.01 × 10⁵ Pa)

P_{H2O(g)} Partial pressure of water vapor (atm)
P_{H2O(g)}^{}* Equilibrium vapor pressure of water at a given temperature (atm)
P_{clay·H2O(s)} Partial pressure of hydrated clay minerals (atm)
R Gas constant (8.3145 J·K⁻¹·mol⁻¹)
RH Relative humidity
S Effective surface area of clay minerals (m²·g⁻¹)
S_{BET} Brunauer–Emmett–Teller (BET) surface area (m²·g⁻¹)
T Absolute temperature (K)
T_p Temperature (°C)
Δu_i Electric potential change of each cation (J·g⁻¹)
ΔU Total change in electric potential energy of cations (J·mol⁻¹)
ΔU_{interlayer} The change in electric potential energy due to hydration at interlayer space of clay minerals (J·mol⁻¹)
ΔU_{surface} The change in electric potential energy due to hydration on the surface of clay minerals (J·mol⁻¹)
V Volume of leachate (mL)
V_{HW} Volume of total hydration water per 100 g mass of dry clay minerals (mL/100 g)
V_{interlayer} Volume of interlayer hydration water per 100 g mass of dry clay minerals (mL/100 g)
z Valence of cation
z_i Valence of cation *i*
β Line broadening at half the maximum intensity of reflection
ε₀ Vacuum permittivity (8.854 × 10⁻¹²C·V⁻¹·m⁻¹)
ε_{is} Relative permittivity of interlayer space
ε_w Relative permittivity of water (80.4)
θ Bragg diffraction angle
λ Wavelength of XRD source (1.5418 Å)
ρ_w Density of water (1.0 mL·g⁻¹)
σ Surface charge density of clay minerals (C·m⁻²)
Δμ The change in chemical potential of hydration reaction (J·mol⁻¹)
τ Particle size of clay minerals in the lamellar direction (Å)

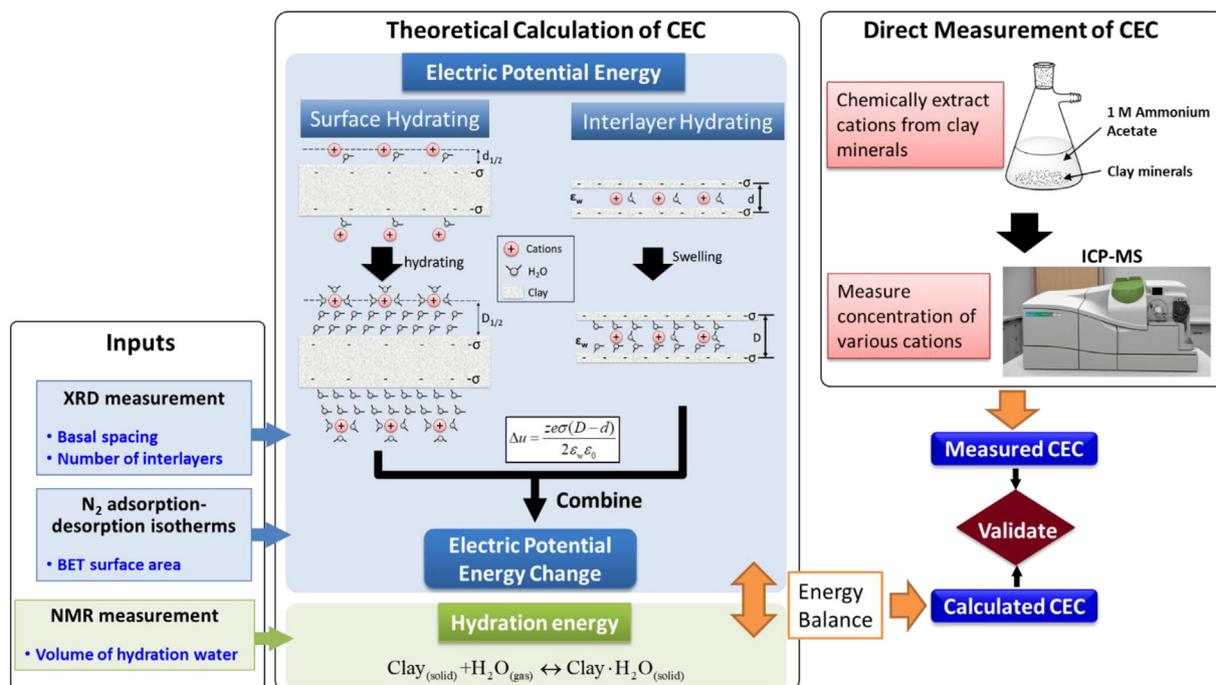


Fig. 1. Workflow of the new NMR-based method for quantifying cation exchange capacity of clay minerals.

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