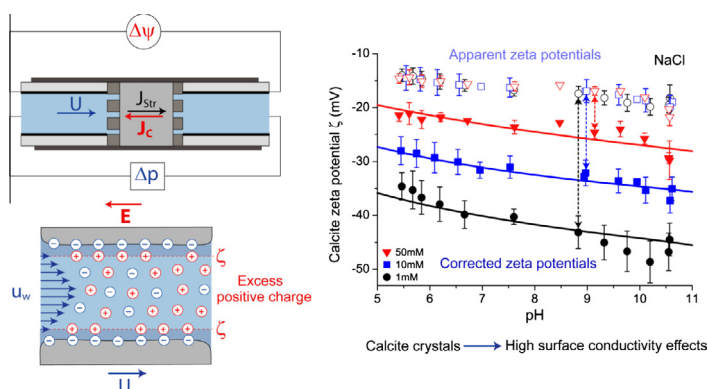# Influence of surface conductivity on the apparent zeta potential of calcite

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GRAPHICAL ABSTRACT

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ABSTRACT

Zeta potential is a physicochemical parameter of particular importance in describing the surface electrical properties of charged porous media. However, the zeta potential of calcite is still poorly known because of the difficulty to interpret streaming potential experiments. The Helmholtz–Smoluchowski (HS) equation is widely used to estimate the apparent zeta potential from these experiments. However, this equation neglects the influence of surface conductivity on streaming potential. We present streaming potential and electrical conductivity measurements on a calcite powder in contact with an aqueous NaCl electrolyte. Our streaming potential model corrects the apparent zeta potential of calcite by accounting for the influence of surface conductivity and flow regime. We show that the HS equation seriously underestimates the zeta potential of calcite, particularly when the electrolyte is diluted (ionic strength $\leqslant 0.01$ M) because of calcite surface conductivity. The basic Stern model successfully predicted the corrected zeta potential by assuming that the zeta potential is located at the outer Helmholtz plane, i.e. without considering a stagnant diffuse layer at the calcite–water interface. The surface conductivity of calcite crystals was inferred from electrical conductivity measurements and computed using our basic Stern model. Surface conductivity was also successfully predicted by our surface complexation model.

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1. Introduction

The calcite–water interface has received ample attention during the past decades due to its high reactive properties and usefulness in many environmental and industrial applications [1,2]. These

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applications include waste water purification [3], nuclear waste and CO_2 sequestration in geological formations [4–6], oil extraction [7], biomineralization [8], and cement and paper production [9,10]. Furthermore, heavy metals and other contaminants can be adsorbed at calcite surface and be incorporated into the calcite crystal structure [11,12]. Adsorption/desorption, dissolution, and precipitation phenomena at the calcite surface can be described by an electrostatic surface complexation model computing the behavior of the electrical double layer (EDL) at the calcite–water interface [1,2].

Accurate acid-base potentiometric titration measurements of the surface charge of calcite cannot be easily performed because of the high reactivity of calcite in water [1,2]. For that reason, electrokinetic experiments like electrophoresis or streaming potential are commonly performed to obtain reliable information on the structure of the calcite EDL [8,11]. The streaming potential method is often used to characterize the electrochemical properties of calcite powders [9,13]. During streaming potential experiments, the sample is subjected to a water pressure difference and the resulting water flow along the particles surface drags the excess of mobile charge of the pore water [14,15]. A shear plane at the particles surface and a macroscopic electrical potential difference, the so-called streaming potential, appear during streaming potential experiments [16,17]. The streaming potential method gives information on the electrical potential at the shear plane, i.e. on the zeta potential if conduction and streaming currents are correctly described [17,18]. The zeta potential can be used to constrain the parameters (sorption equilibrium constants, capacitance(s)) of the electrostatic surface complexation model [1,2].

However, the conversion of streaming potential measurements into zeta potentials is not straightforward because two effects, one associated with the surface conductivity of the material, and the other associated with the flow regime, decrease the streaming potentials [18,19]. The Helmholtz–Smoluchowski (HS) equation neglects these two effects and its use can lead to underestimate zeta potentials [16,20]. Heberling et al. [9,10] used the HS equation to interpret their streaming potential experiments on a calcite powder in terms of apparent zeta potentials. Nevertheless, the HS equation can only be used when surface conductivity can be neglected and in the case of viscous laminar flow [16,20]. Streaming potential induces electromigration currents in the EDL at the surface of the particles, which are responsible for surface conductivity [17,18]. Surface conductivity increases conduction current opposed to streaming current and hence decreases the magnitude of the streaming potential [17,19]. Inertial laminar flow decreases the apparent permeability, water flow in the pores and the resulting streaming potential [16,21]. Given these observations, one may question whether the HS equation is appropriated to estimate the zeta potential of calcite powders from streaming potential experiments.

In the double layer theory, the zeta potential is considered to be located very close to the beginning of the diffuse layer [18,19]. The viscosity of the diffuse layer is assumed to be equal to the viscosity of the bulk water and the liquid viscosity between the solid surface and the beginning of the diffuse layer is assumed to be significantly higher than the viscosity of the diffuse layer [19,22]. Water flow along the particle surface is considered in the diffuse layer and bulk water and no water flow is considered between the solid surface and the beginning of the diffuse layer [18,23]. This is the reason why it is assumed that the shear plane is located at the beginning of the diffuse layer in the double layer theory. Heberling et al. [9,10] considered the presence of a stagnant diffuse layer at the calcite–water interface, i.e. a shear plane several nanometers away from the beginning of the diffuse layer, to reconcile high electrical potentials at the beginning of the diffuse layer computed by their surface complexation model to low measured apparent zeta

potentials (the magnitude of the computed electrical potential decreases with the distance from the surface). Furthermore, on the contrary to silica where protruding polysilicic acid groups may increase the distance between the beginning of the diffuse layer and the shear plane [23,24], there is no physical reason explaining the presence of a stagnant diffuse layer at the calcite surface. Heberling et al. [9,10] also assumed that the thickness of the stagnant diffuse layer decreases with increasing salinity. This assumption is a typical signature of surface conductivity effects because the influence of surface conductivity on electrokinetic experiments decreases when salinity increases [25–29]. For instance, Heberling et al. [9,10] assumed that the shear plane can be as far as 100–150 Å and 30–40 Å from the beginning of the diffuse layer at salinities of 10^{-3} M and 10^{-2} M NaCl, respectively. The location of the shear plane predicted by the surface complexation model of Heberling et al. [9,10] is not in agreement with the double layer theory. Their use of the HS equation to interpret streaming potential experiments may explain why these authors considered low apparent zeta potentials and a large stagnant diffuse layer at low ionic strengths.

Revil and co-workers [14–16,20] developed streaming potential models accounting for surface conductivity and Reynolds number effects. The Reynolds number is the ratio between inertial and viscous forces in the Navier–Stokes equation. Crespy et al. [20] successfully interpreted their streaming potential and electrical conductivity experiments on glass beads in contact with a NaCl solution in terms of low apparent and high corrected zeta potentials. Crespy et al. [20] showed considerably high surface conductivity and Reynolds number effects for glass beads pack immersed in a dilute electrolyte (salinity < 0.01 M) and large glass beads (size > 1000 μm), respectively. Nevertheless, Crespy et al. [20] did not use an electrostatic surface complexation model to interpret their streaming potential and conductivity measurements, thus their interpretation of streaming potentials in terms of surface complexation reactions is limited.

To the best of our knowledge, no study has used streaming potential, electrical conductivity measurements and an electrostatic surface complexation model to obtain the zeta potential and describe the behavior of the electrical double layer of calcite. After a brief theoretical description of the streaming potential, conductivity and surface complexation models, the zeta potentials of a calcite powder inferred from streaming potential and conductivity measurements are successfully reproduced by our basic Stern model (BSM). No assumption of a stagnant diffuse layer at the calcite surface is considered. Special care is given to the description of the surface processes responsible for the surface conductivity of calcite crystals.

2. Theoretical background

2.1. Streaming potential model

During streaming potential experiments, the sample is sandwiched between two water compartments, and the imposed water pressure difference induces a water flow and a shear plane at the particles surface [23,30] (Fig. 1). The zeta potential is the electrical potential located at the shear plane [18,19]. Water flow also drags the excess counter-ions in the diffuse layer along the pores surface and creates a macroscopic current density, the streaming current and a macroscopic electrical potential difference, the streaming potential [14,17]. The electrical field induced by the streaming potential is responsible for conduction currents in the bulk pore water and in the EDL. The surface conductivity of the particles increases the conduction current density, which is opposed to