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X-ray Crystal Truncation Rod Profiles of the Calcite/Artificial Sea Water Interface

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1 Introduction

Imbibition of low salinity artificial sea water (ASW) into a porous chalk rock spontaneously enhanced oil recovery from some chalks [1]. However, the mechanism has not been well understood. We considered that the wettability alteration of the calcite ($CaCO_3$) surface, which is the main constituent of chalk, induced by ion exchange can stimulate desorption of oil molecules from the surface. The wettability alteration from oil to water wet by exchanging the surface $CaCO_3$ ion pairs to $MgSO_4$ pairs dissolved in ASW was predicted by our theoretical simulations based on density functional theory (DFT) [2].

Here we performed specular X-ray crystal truncation rod (CTR) scattering measurements to reveal the interfacial structure of $CaCO_3$ (calcite)/ASW interfaces. Assuming that ion exchange occurs at the surface as predicted by our DFT study, the CTR scattering profile should change for some compositions of ASW.

2 Experiment

The natural cleavage plane of calcite ($CaCO_3$) is {10.4} in the hexagonal cell setting. The specular X-ray CTR scattering for the {10.4} surface immersed in ASW were measured at Photon Factory, KEK, Japan (BL-4C). Aqueous NaCl solution (0.5 mol/L) was used as a model for ASW. A thin film liquid cell was used for the experiments and the liquid surface was covered by a thin polyimide film to prevent the solution from evaporating. The CTR profiles were measured by rocking scans at given {*h*0.*l*} values, where *h* is equal to *l*/4 with monochromatic X-ray beam with an energy of 11.0 keV. The integrated and background corrected scattering intensities were supsequently corrected for Lorentz, polarization, attenuation factors, and rod interception effect. The wettability of the calcite surface is temperature dependent [1,3]. Therefore, the measurements where performed at specific sample temperature:s 25, 45, and 70°C. A new sample cell was developed to make the high-temperature experiment in this thin-film configuration possible.

3 Results and Discussion

The measured CTR profiles for the calcite/0.5 M NaCl (aq) interface are plotted in Fig. 1. Two Bragg peaks were observed at l = 4 and 8 which correspond to the (10.4) and (20.8) planes. The intensities between these Bragg peaks at around l = 6 reflect the interfacial structure. The intensities at l ~ 6 showed no significant difference at increased temperature from 25 to 70°C. This implied that the interfacial structure would not change by increasing temperature in this system. Further analysis is necessary for deriving the specular interfacial electron density profiles over the interface.

4 Summary

High-temperature experiments for a calcite {10.4}/NaCl (aq) interface were performed by using a newly developed sample cell. The observed CTR profile at 70°C showed no significant difference from the room temperature profile. The effect of Mg^{2+} and SO_4^{2-} will be investigated in future experiments.

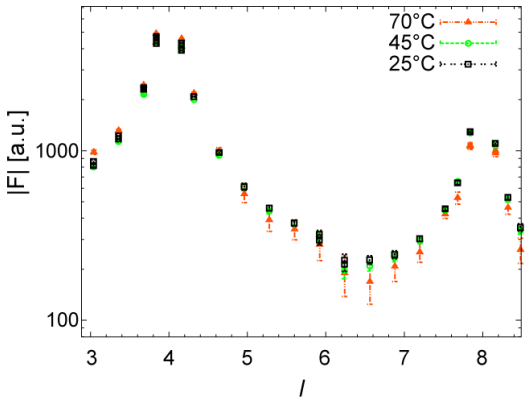

Fig. 1: X-ray CTR scattering profiles for calcite/0.5M NaCl (aq) interface at 25, 45, and 70°C. The vertical axis indicates the absolute values of structure factor *F* in an arbitrary unit. The horizontal axis indicates the *l* values of the Miller indices.

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References

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