Characteristics of produced waters and biogeochemical processes for effective management using constructed wetland treatment systems

J.H. RODGERS, JR. AND J.W. CASTLE*

Clemson University, Clemson, SC 29634, USA
(jrodger@clemson.edu,
*correspondence: jcastle@clemson.edu)

Waters associated with energy production, including extraction of oil and natural gas, may require renovation prior to discharge or reuse. Treatment of these waters to transfer or transform constituents of concern may limit production at marginal sites. Constructed wetland treatment systems can treat a variety of constituents to achieve performance criteria for discharge or reuse in many situations. A wide range of chemical, physical, and risk characteristics are present in produced waters. Produced waters can range from fresh to hypersaline. Cations found in produced waters commonly include sodium, calcium, magnesium, and potassium; anions present often include chloride, sulphate, and bicarbonate. Reverse osmosis (RO) is sometimes used to reduce concentration of the cations and anions. However, specific constituents can pass through RO membranes and require further treatment. One of these constituents is ammonia, which may be treated through nitrification and denitrification. Metals that are of concern in produced waters can include any or all of the following: iron, manganese, zinc, cadmium, copper, lead, nickel, zinc, and others. These metals in produced waters can be treated through specific biogeochemical processes such as oxidation and reduction. Other constituents of concern identified in produced waters include arsenic and selenium. These ‘metalloids’ are amenable to treatment in specifically designed constructed wetland systems through targeted biogeochemical processes. Produced waters can contain a range of organic constituents from oil and grease to low molecular-weight aromatic hydrocarbons. Concentrations of dissolved and dispersed organic constituents can be decreased by oxidation.

Depending on the designated post-treatment use for a produced water and its composition, various combinations of inorganic and organic constituents can be specifically targeted for treatment in constructed wetland systems. To achieve treatment of targeted constituents, constructed wetland systems are designed to promote specific biogeochemical processes including oxidation, reduction, nitrification, and denitrification.

The mechanism of ACC nanoparticle transformation to vaterite

J.D. RODRIGUEZ-BLANCO[1], P. BOTS[1], N.J. TERRILL[2], S. SHAW[1] AND L.G. BENNING[1]

[1]School of Earth and Environment, Univ. of Leeds, Leeds. LS2 9JT, UK (j.d.rodriguez@see.leeds.ac.uk)
[2]Diamond Light Source Ltd, OX11 0DE, UK

The formation of calcium carbonate ($CaCO_3$) minerals is a key part of the global carbon cycle. Crystalline $CaCO_3$ phases (e.g. vaterite, calcite) often form via a poorly-ordered metastable precursor, amorphous calcium carbonate (ACC). The transformation of ACC nanoparticles to the $CaCO_3$ polymorphs vaterite (Vat) is usually extremely fast i. e., seconds - minutes. Here we demostrate the use of an *in situ* time-resolved synchrotron-based scattering approach (i. e. SAXS/WAXS) combined with SEM imaging to quantify the fast kinetics and mechanisms of Vat crystallization.

Experiments were carried out on station I22 at the Diamond Light Source, UK. The precipitation of ACC was induced by mixing molar solutions of Ca^{2+} and CO_3^{2-} at 20°C and the crystallization was monitored via simultaneous SAXS/WAXS patterns acquisition at 1s time frames. In addition the effects of Mg^{2+} and SO_4^{2-} on the crystallization reactions were studied.

The WAXS data (Fig 1, 3D plot) shows that the transformation from ACC to Vat occurred within ~100s. The SAXS patterns revealed that the initial spherical ACC nanoparticles (~36nm) transform to Vat nanoparticles (~10nm) which agrregate to form ~1µm clusters. The crystallization of these Vat nanoparticle subunits likely occurs via an internal reordering and dehydration process. The aggregated Vat crystallites then continue to grow via Ostwald ripening until they reach ~50nm in size (after ~ 3000s). These sizes were confirmed via SEM observations (Fig 1, insets at right).

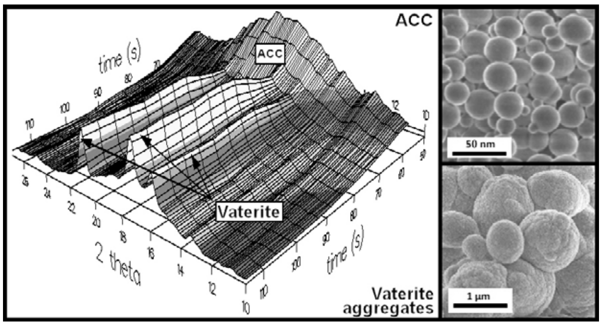

Figure 1: 3D WAXS plot and SEM images showing ACC-Vat transformation.