Dephasing proton spins on DOLLOP surfaces with strong magnetic gradients

1. Motivation

Claims that passing hard water through a magnetic field somehow influences the structure and morphology of the calcium carbonate after subsequent precipitation have been met with skepticism within the scientific community due to the absence of a plausible mechanistic explanation. This situation changed when investigations of $CaCO_3$ nucleation uncovered the existence of thermodynamically stable liquid-like prenucleation clusters [1]. Coey [2] then showed that these nanometer-scale clusters provide the basis for a plausible mechanism for magnetic treatment. These two discoveries are of imminent importance for the drinking water industry, since the ratio of Ca^{2+} in DOLLOPs compared to the overall Ca^{2+} concentration does not only provide a completely new physical water quality parameter, but by influencing it by magnetic treatment can change water parameters like conductivity and ion strength, opening the door to sustainable, low-cost and additive-free water treatment.

2. Background

In 2012 Coey [2] proposed a theory on the mechanism of magnetic water treatment based on the gradient of the applied field rather than its absolute strength. In this theory the most recent discoveries about the crystallisation dynamics of Calcium carbonate are taken into account, namely the so-called DOLLOPs (dynamically ordered liquid like oxyanion polymers) which form a colloidal phase of Calcium carbonate prenucleation clusters accounting up to 50% of calcium present in an aqueous solution of calcium bicarbonate [3]. They aggregate into larger particles (up to about 100 nm) and form a liquid emulsion [4]. Coey [2] describes how a magnetic field gradient can act on the DOLLOPs, which could account for the so-called “magnetic memory” of water. He shows that contrary to pure mechanical stress, which is unable to induce changes to the structure of DOLLOPs directly, a magnetic field gradient can act on the DOLLOP surface and affect its growth dynamics.

3. State of the art

Bicarbonate ions, the predominant carbonate species in solution at neutral pH, are considered to sit next to each other on one side of a polar nucleation cluster and form the negatively charged surface. The other, positive, side is occupied by Ca^{2+} ions. For the cluster to grow on the negatively charged side, protons in the HCO_3^- ions must be replaced by Ca^{2+} ions. It is upon these protons that the magnetic field acts: An inhomogeneous magnetic field, *i.e.*, gradients in the magnetic field, can force the exchange of singlet and triplet states of the proton spin dimers present in the HCO_3^- layer, thereby facilitating their replacement by Ca^{2+} ions. This facilitation is achieved by spin-dephasing of a proton dimer induced by the magnetic field gradient, because proton spins precess at different rates at different field strengths. More exactly, the proton spins precess in a given field B at the Larmor frequency f_pB (f_p = 42.6 $MHzT^{-1}$). In order to dephase the spins in a proton dimer; they must precess at different frequencies so that the accumulated phase difference $\Delta\phi$ fulfils the condition

$$\Delta\phi \geq \pi \quad (1)$$

Based on this inequality Coey [21] derived a condition for an appreciable magnetic field effect, by the use of which the effectiveness of the magnetic fields in this work will be analyzed,

$$C = 2\frac{L}{v} f_p a \nabla B \geq 1 \quad (2)$$

where C is the Coey criterion, L the length of the magnetic device, v the velocity of the DOLLOPs, f_P the Larmor frequency of a proton, a the spin separation (0.25 nm) and ∇B the magnetic field gradient. If $C \geq 1$, then the magnetic device can effectively influence the crystallization of calcium carbonate.

This theory was successfully tested [5] by measuring the effect of very weak field magnets (< 10 G) containing strong magnetic inhomogeneities ($\nabla B = 2\ kG \cdot m^{-1}$) on tap water samples by the use of electric impedance spectroscopy (EIS) and laser scattering. The results can be interpreted as an enhanced formation of DOLLOPs, mesoscale prenucleation clusters, due to exposure to an appropriate magnetic field, consistent with Coey's theory.

4. Research challenge

The goal of this project is to learn more about the time constants of the magnetic treatment of aqueous $CaCO_3$ solutions. Therefore, first the tap water experiments described in [5] will be repeated with the Ca^{2+} concentration monitored by a Ca^{2+} selective electrode. Then titration experiments with artificial solutions as described in [1] will be carried out with and without magnetic field influence. Optionally these experiments will be repeated with magnetic devices other than those used in [5]. Finally, chemical additives will be used in order to achieve similar results as with the magnetic field treatment in order to make the method comparable to established chemical antiscalants.

5. Requirements

The ideal candidate has a BSc degree in physical chemistry, chemistry or physics with experience in wet chemistry and a solid knowledge about the physics of magnetism. Knowledge about statistics is an advantage.

6. Partnership

This research project is part of the Wetsus research theme Applied Water Physics in collaboration with the Department of Chemistry, University of Konstanz, Germany. The student will do most of the experimental work in Konstanz.

7. Application

If you are interested in this project, please contact PD Dr. Denis Gebauer (denis.gebauer@uni-konstanz.de) or Dr. Elmar C. Fuchs (elmar.fuchs@wetsus.nl) for more information or directly apply by sending your CV to the same address. The internship/MSc thesis includes a reimbursement for living expenses of 350 euro per month.

8. References

[1] Gebauer, D.; Völkel, A.; Cölfen, H.; Stable prenucleation calcium carbonate clusters, *Science* **322** (2008) 1819-1822

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