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Influence of static magnetic field on the kinetics of calcium carbonate formation

D. Myśliwiec [a], A. Szcześ [b,*], S. Chibowski [a]

[a] Department of Radiochemistry and Colloid Chemistry, Faculty of Chemistry, Maria Curie-Sklodowska University, Maria Curie-Sklodowska Sq. 3, 20031 Lublin, Poland
[b] Department of Physical Chemistry—Interfacial Phenomena, Faculty of Chemistry, Maria Curie-Sklodowska University, Maria Curie-Sklodowska Sq. 3, 20031 Lublin, Poland

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ABSTRACT

The effect of reactants concentration on the kinetics of calcium carbonate precipitation via sodium carbonate and calcium chloride solutions mixing in the absence of external magnetic field (in geomagnetic field—GMF) and in static magnetic field (MF) is investigated for different concentrations of salts: 0.005 M, 0.01 M and 0.02 M at 25 °C.

Absorbance and conductivity measurements indicate the mechanism of precipitation strongly depends on the concentration of the solutions. MF does not affect the yield of precipitation as well as the mechanism of precipitation. However, for the 0.01 M and 0.02 M the rate of precipitation increased in MF.

Introduction

Damage caused by scale formation is a problem which prevails in many industries and households. Equipment damage and decrease in flow rates is a source of financial loss and therefore methods to prevent or remove scale formation have considerable financial impact. One of method to prevent scaling is use of magnetic fields (MF). Application of external MF in flow systems greatly effects calcium carbonate precipitation and it was extensively studied in recent years [1–31]. In all cases, the reference system was not exposed to an external MF.

In many industrial systems, only a small section of the flow is exposed in the MF and the crucial parameter is mainly the flow rate [6–8,10,11,14–20,24–26,28]. In addition, MF can be applied in static solutions after a certain lapse of time [1–5,9,13,19,21,23,27,30]. An exposure may take place before the process [1–5, 7–11,15,16,23,25,26] or immediately with the flow [13,14,18, 19,27,28,30].

Higashitani et al. [1] showed that static MF decreases the nucleation rate and accelerates the crystal growth of calcium carbonate precipitated in sodium carbonate and calcium chloride solution and the concentration of aragonite is enhanced compared with the flow conditions without any MF The MF effects are profound in sodium carbonate solutions and they increase with MF intensities and exposure time up to certain values (saturation effects). Magnetic effects in water solutions can be maintained up to six days after the application of MF [1,29]. Experimental results indicate that not only the strength of the MF, but also way of exposition to a MF and the design and configurations of magnetic treatment devices, as well as their location may significantly affect the results [32,33].

An impact of MF on zeta potential, diffusivity and coagulation rate of some colloidal systems was observed too [2–17]. However, in some studies no changes were observed from the MF action [18,19]. The reason is still unknown. One of the possible explanations may be differences in the exposing methods.

During the recent 20 years researchers shown that MF may affect other physicochemical parameters of the system where precipitation of calcium carbonate occurs. MF increases conductivity of water and electrolytes solutions as well as influences the evaporating rate [20]. In the case of electrolyte solutions the difference strongly depends on the nature of the ions present in the solution Chibowski et al. [21] reported a reduction in adhesion of the in situ precipitated calcium carbonate to various solid surfaces. In fact other authors proved that homogenous precipitation is favored in MF [24–26]. According to Lundager Madsen [22,27,30],

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[*] Corresponding author. Tel.: +48 81 537 77 47; fax: +48 81 533 33 48.
E-mail address: aszczes@poczta.umcs.lublin.pl (A. Szcześ).

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MF may affect precipitation only in case of diamagnetic metal ions in solutions of weak acids anions. The proposed mechanism is based on proton transfer from water to a salt, i.e., MF can interact with the proton spin, changing significantly thus its relaxation time. MF effects were only observed in ordinary water, not in heavy water [30]. Alternative explanation was proposed by Higashitani et al. [2]. They postulate that experimental changes are results of disturbances in electrical double layers, in particular structure of dipoles of water in hydration shell of an ion might be altered. This mechanism could explain the effect of different ions in water's physicochemical constants under an external magnetic field [4,20]. For many years it was believed that those two mechanisms are opposite to each other. However one of the most important conclusions from the series of papers by Chibowski and coworkers is that they are rather complementary [4–8,20]. Quantum mechanical theoretical models supported by experimental evidences indicate that the energy of an MF can be stored in coherently exited water molecular rotors (memory effects), altering at the same time the ground thermodynamics state of water solutions, modifying thus basic thermodynamic processes [17,34], which determine the amount of energy transferred from MF to a solution. As a result the initial stages of crystallization are changed and relative concentration of aragonite is increased [1,11,16,19,31].

Although magnetic water treatment has been used for many years as a non-chemical method to prevent scaling, there are still some open questions on this issue. The aim of this paper is the evaluation of the effect of reactants concentration on the kinetics of calcium carbonate precipitation, mixing of sodium carbonate and calcium chloride solutions in a static magnetic field. The kinetics of precipitation was determined by measuring the conductivity changes versus time during calcium carbonate precipitation. Moreover, the statistical processing of results evaluated the importance of the MF on the kinetic reactions. The results interpret the controversy in this subject that appears in the literature.

Experimental

Chemicals and magnets

The salts were of 'per analysis' grade from Avantor Performance Materials Poland S.A. The water used was purified by a Milli-Q plus water purification system (Millipore, USA) with a resistivity of 18.2 MΩ cm. Three concentrations of salts were examined 0.005 M, 0.01 M and 0.02 M.

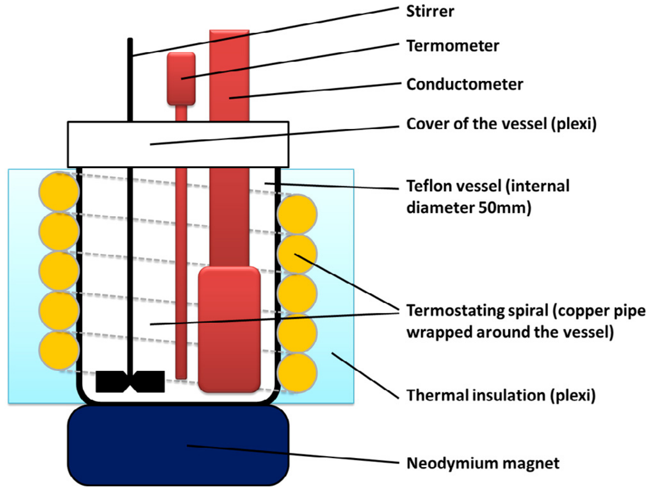
In this experiment cylindrical neodymium magnets of 55 mm diameter and 10 mm high were used (ENES Magnesy Paweł and Tomasz Zientek, Poland). The strongest field is generated close to the surface of the magnet (bottom of the flask), where the induction of magnetic field measured by the Gauss Meter (Gauss/Tesla Meter 5070 by F.W. Bell) equals to 240 mT in a geometrical centre of the magnet surface.

Experimental setup

Simplified scheme of the experimental setup is shown in Fig. 1.

The MF was applied on the bottom of the Teflon vessel, which was in contact with a surface of the neodymium magnet. Thermometer was covered with Teflon to isolate its' material from the solution. All measurements were done at 25 °C ± 2° and all solutions were equilibrated in a thermostating bath for 30 min before experiment. For comparison, measurements were made without an external MF and the solution was exposed only to GMF.

Absorbance and conductivity experiments were performed according to the procedure: .40 mL of $CaCl_2$ and Na_2CO_3 were placed inside an experimental vessel and immediately vigorous stirring was applied. Conductivity measurements were done every 30 s up to 75 min at 0.01 M and 0.02 M and 120 min for 0.005 M.



*) additional aperture was made in the cover of the vessel as an inlet for solutions

Fig. 1. Scheme of the experimental setup.

Optical absorbance experiments were carried out from 700 to 200 nm using Carry 300 UV–vis spectrometer (Varian) equipped with flow cell and results at 550 nm are reported. In the MF experiments solutions were not exposed to the field prior to mixing. Conductivity and absorbance data represent average values from 2 to 4 and 3–8 experimental trials, respectively.

Following equilibrium (75 min for 0.01 M and 0.02 M solutions, 120 min for 0.005 M solutions) the precipitates were filtered with cellulose filter having of 0.45 μm pores, washed with a distilled water and dried in desiccator for 48 h at room temperature. Samples were then analyzed with SEM (Quanta 3D FEG, FEI) and Raman spectroscopy (inVia Reflex instrument, Renishaw, UK).

Uncertainties and statistical analysis

Statistical approach was applied to calculate single point uncertainty [35]:

$$\mathrm{MU} = \frac{\mathrm{SD}}{\sqrt{n}} \cdot t_{0.05,n-1} \qquad (1)$$

where MU is measurement uncertainty, SD stands for standard deviation, n is a number of replicates, and $t_{0.05;n-1}$ is a parameter of the t-Student distribution at 95% confidence interval. Grubbs test for outliers was performed before the uncertainty was calculated [35]. Wherever two values or two sets of values are compared a Student's *t*-test is performed (independent for values, paired for sets) [36,37]. If it is not stated the confidence interval of a statistical test is equal to 95%.

Results and discussion

Conductivity experiment

Fig. 2 shows the conductivity changes with time for MF treated and untreated solutions at different concentration. MF significantly affects values of conductivity only for 0.02 M solutions.

In general, nanoparticle synthesis from solutions can be divided into two stages: nucleation (which is very fast) and crystal growth which occurs by two primary mechanism: Ostwald ripening