Polymorphic and morphological transformations of CaCO_3 under CO_2 atmosphere and under the Influence of EDTA at 60 °C.

S. Bhuvaneswari¹, K. Palanisamy², K. Subramani¹ and V.K. Subramanian^{2*}

¹Department of Chemistry, Islamaiya College, Vaniambadi, Tamilnadu

²Department of Chemistry, Annamalai University, Annamalainagar, 608 002 Tamilnadu.

E-mail address: drvksau@gmail.com

Keywords: Scale, Crystal growth, Calcite, Morphology

Abstract. Calcium carbonate scale samples were synthesized from calcium chloride solution in the presence of ethylenediaminetetraacetic acid (EDTA) by bubbling CO_2 gas. Samples were prepared with different concentrations of EDTA at 60 °C and characterized using XRD, FTIR and SEM techniques. The details revealed that EDTA stabilizes aragonite more efficiently at higher concentrations of EDTA. It was also observed that increasing the concentration of EDTA has no significant impact on the polymorphic specificity where as influence the morphology and the size of the particles.

1. INTRODUCTION

Calcium carbonate (CaCO_3) one of the most common mineral has many industrial uses such as fillers, dentifrices, and has great biological role as structural supports in skeletons [1-8]. Hence the morphological and polymorphic studies of CaCO_3 under various conditions have gained much importance in the past few decades. Calcium carbonate exhibit six polymorphic forms; three hydrated forms (amorphous calcium carbonate, calcium carbonate hexahydrate, calcium carbonate monohydrate) and three anhydrous polymorphs (calcite, aragonite and vaterite) [9–14].

CaCO_3 is also found in a major fraction in the scale formed in heat exchanger equipments. Of the various polymorphs of CaCO_3 calcite (rhombohedral structure) and aragonite (orthorhombic) [15] are often found in the scale where as Vaterite (hexagonal) is seldom found. The reason for this is that vaterite is the least stable and aragonite is metastable and calcite is the most stable form. Due to this reason, vaterite gets converted into calcite in due course of time following the 'step rule'. Earlier reports suggest that the crystal structure and morphology depend on several parameters such as supersaturation, solvents, additives, etc [16-21].

Prevention of scaling can be achieved by physical and chemical techniques [22]. Addition of chemical reagents like chelating agents is one of the most common practices in internal water treatment process [23]. These chelating agents form complex with Ca^{2+} and other scale forming ions and inhibit the formation of scale to a great extent [17-20].

Though there are many reports on the synthesis of CaCO_3 , most of them are by direct addition of a carbonate solution into a calcium solution. Here in this work, we report the synthesis of CaCO_3 from CaCl_2 by bubbling CO_2 gas. The experiments were carried out in the presence of EDTA at 60°C. The details of the findings reveal that EDTA has a marked influence on controlling the polymorphic composition in the sample.

2. EXPERIMENTAL PROCEDURES:

2.1 Materials

Analytical grade CaCl_2 and EDTA were obtained from Hi-media. De-mineralized water was used for the preparation of aqueous solutions. The reagents were used as such. Double distilled water was used to make all aqueous solutions. Analytical grade hydrochloric acid and sodium hydroxide were used to adjust the pH whenever necessary. Experiments were conducted at pH 7. CO_2 gas was obtained in a cylinder from Inox Ltd.

2.2 Preparation of CaCO_3

CaCO_3 was crystallized by a modified method from a described one [24]. A typical procedure is as follows: 50 ml 0.1 M CaCl_2 , 20 ml of 0.1 M EDTA were consecutively added in a round bottom flask, connected to a water condenser and heated using a rotamantle having a thermostat control with accuracy $\pm 1^\circ\text{C}$. The rotamantle was then heated to 60°C . After attaining the temperature for 15 minutes, CO_2 gas was passed through the solution at a pressure of 1 atm for 2 h. and digested at the same temperature for 24 h. After digestion the sample was filtered, washed with distilled water and then dried at 45°C in an oven. A schematic representation of the experimental set up is provided in Fig. 1.

Fig. 1. Schematic representation of the experimental set up

2.3 Characterization

The structure of the samples was confirmed by FTIR, Raman spectroscopy and XRD methods and the morphological studies were done using SEM and FESEM. FT-IR spectra were taken in the range 500 to 4000 cm^{-1} using Avatar-330 FTIR and JASCO-5300 FTIR instruments after pelletizing with KBr. Raman spectra of the samples were obtained with the WI Tec Confocal Raman Microscope alpha 300 R Raman spectrometer, excited by laser line having a wavelength of 488nm , provided by an argon laser. The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advanced XRD diffractometer with Cu K α radiation at $\lambda = 1.5406\text{ \AA}$. Microscopic morphological images were taken using Philips XL30 -ESEM Scanning Electron Microscope (SEM) using a beam voltage of 20 kV and FESEM CARL ZESIS with In lens detectors. The samples were coated with gold prior to imaging.

3. RESULTS AND DISCUSSIONS

It is well known that different crystal forms of CaCO_3 shows different bands in FTIR spectrum [25-27]. The polymorphic composition of calcium carbonate crystals were identified by FTIR. The reference bands observed around 700 - 745 , 874 , 1435 - 1418 cm^{-1} were assigned to the in-plane bending (ν_4), out-of-plane bending (ν_2), and asymmetric stretching (ν_3) modes of CO_3^{2-} , respectively. The FTIR patterns of samples prepared at 60°C with different concentrations of EDTA are presented in Fig. 2, 3 and 4 respectively. It is obvious from the images that invariably all the samples contained calcite. Characteristic peaks of calcite were prominent in all samples at 713 , 875 and 1476 cm^{-1} . Only samples prepared with 20 ml (Fig. 2 c) and 30 ml (Fig. 2 d) EDTA contained a shallow peak at 700 indicating presence of aragonite. For confirming this, spectra is deconvoluted and is presented in Fig. 3.

Fig. 2. FTIR of CaCO_3 synthesized at 60°C . (a) Blank, (b) EDTA 10 ml, (c) EDTA 20 ml(d) EDTA 30 ml

Fig. 3. Deconvoluted FTIR of CaCO_3 synthesized at 60°C .

These observations are further confirmed by XRD. The XRD patterns of the samples prepared with different concentrations of EDTA and blank at 60°C are presented in Fig. 4. It is evident from the presence of characteristic peaks of calcite at $2\theta \sim 29.4$ (104) that invariably all the samples contained calcite. As observed in the case of FTIR, aragonite was found to be present in very little mole fraction in samples prepared at 60°C with 20 ml and 30 ml EDTA (Fig. 6 b,c). The presence of aragonite was confirmed by the appearance of low intensity peaks at $2\theta \sim 26.2$ (111).

Fig. 4. XRD of CaCO_3 synthesized at 60°C . (a) Blank, (b) EDTA 10 ml, (c) EDTA 20 ml(d) EDTA 30 ml

Fig. 5 depicts the SEM images of the sample prepared at 60°C . The morphology of the sample prepared without EDTA (Fig. 5 a, b) is found to be rhomboidal and confirmed to be that of calcite as calcite alone was present in this sample. The morphology of samples prepared with 10 ml of EDTA is presented in Fig. 5c and d. It is obvious that the rhomboidal blocks of calcite are the major constituent in the image. There are few spherical morphology also observed in the sample. The XRD pattern confirmed the presence of calcite alone in these samples too. Hence the morphology could be assigned to calcite only.

Another reason could be that the corners and edges of the rhomboidal structures are rounded off due to the presence of EDTA. This phenomenon of rounding of the edges and corners are characteristics of redissolution of crystallites [28]. This became more severe as the concentration is further increased to 30 ml (Fig. 5 g, h). It could be seen only spherical particles in this case which the usual morphology of vaterite is. But the XRD and FYTIR data indicated that calcite is the major constituent with very little aragonite. This indicates that as the concentration of EDTA increases it could significantly influence the crystallization behavior of CaCO_3 .

Fig. 5. SEM of CaCO_3 synthesized at 60°C . (a, b) Blank, (c, d) EDTA 10 ml, (e, f) EDTA 20 ml, (g,h) EDTA 30 ml

4. CONCLUSION

The studies carried out to understand the effect of EDTA on the crystal growth, polymorphism and morphology of the CaCO_3 synthesis from CaCl_2 by CO_2 bubbling has resulted in to the following conclusions. Firstly, the optimum concentration of EDTA is 20 ml. Secondly, the morphology of CaCO_3 is affected by the presence of EDTA and rounding of the corners and edges are observed and at higher concentrations, the morphology is less uniform. Thirdly with higher concentrations presence of aragonite was observed. These results are of importance in water treatment associated with return line treatment from boilers, where EDTA is used to control scale formation.

References

- [1] J.L. Addadi and S. Weiner, *Angew. Chem., Int. Ed. Engl.*, 1992, 31, 153.
- [2] J. A. H. Oates, *Lime and Limestone: Chemistry and Technology, Production and Uses*, Wiley-VCH, Weinheim, 1998.
- [3] B. R. Heywood and S. Mann, *Adv. Mater.*, 1994, 6, 9.
- [4] S. Weiner and L. Addadi, *J. Mater. Chem.*, 1997, 7, 689.

-
- [5] A. Berman, J. Hason, L. Leiserowitz, T. F. Koetzle, S. Weiner and L. Addadi, *Science*, 1993, 259, 776.
- [6] S. Mann, *J. Mater. Chem.*, 1995, 5, 935.
- [7] S. Mann and G. A. Ozin, *Nature*, 1996, 382, 313.
- [8] H. Lowenstam and S. Weiner, *On Biomineralization*, Oxford University Press, New York, 1989.
- [9] T. Chen, A. Neville, M. Yuan, *J. Pet. Sci. Eng.* 46 (2005) 185.
- [10] H.A. El Dahan, H.S. Hegazy, *Desalination* 127 (2000) 111–118.
- [11] Y. Tang, W. Yang, X. Yin, Y. Liu, Y.P. Yin, J. Wang, *Desalination* 228 (2008) 55–60.
- [12] K.D. Demadis, E. Mavredaki, A. Stathouloupoulou, E. Neofotistou, C. Mantzaridis, *Desalination* 213 (2007) 38–46.
- [13] S.J. Dyer, G.M. Graham, *J. Pet. Sci. Eng.* 37 (2003) 171–181.
- [14] J.Y. Gal, Y. Fovet, N. Gatche, *Water Res.* 36 (2002) 755.
- [15] L.N. Plummer, E. Busenberg, The solubilities of calcite, aragonite and vaterite in CO₂–H₂O solutions between 0 to 90 °C, and an evaluation of the aqueous model for the system CaCO₃–CO₂–H₂O, *Geochim. Cosmochim. Acta* 46 (1982) 1011–1040.
- [16] Dong-Ki Keum, Kensuke Naka, Yoshiki Chujo Unique crystal morphology of hydrophobic CaCO₃ composite by sodium trisilanolate in a mixture of a water-miscible organic solvent and water *Journal of Crystal Growth* 259 (2003) 411–418
- [17] L.B. Gower, D.J. Odom, *J. Crystal Growth* 210 (2000) 719.
- [18] W. Wang, G. Wang, Y. Liu, C. Zheng, Y. Zhan, *J. Mater. Chem.* 11 (2001) 1752.
- [19] K. Naka, Y. Tanaka, Y. Chujo, Y. Ito, *Chem. Commun.* (1999) 1931.
- [20] K. Naka, D.K. Keum, Y. Tanaka, Y. Chujo, *Chem. Commun.* (2000) 1537.
- [21] F. Manoli, E. Dalas, *J. Crystal Growth* 204 (1999) 369.
- [22] F. Alimi, M. Tlili, C. Gabrielli, M. Georges, M. Ben Amor, Effect of a magnetic water treatment on homogeneous and heterogeneous precipitation of calcium carbonate, *Water Res.* 40 (2006) 941–950.
- [23] [20] T.Y. Chen, S.H. Chan, Novel biological inhibitors of fouling and scale formation on heat transfer surfaces through genetic engineering, *Microscale Thermophys. Eng.* 4 (2000) 103–108.
- [24] D. Lisitsin, Q. Yang, D. Hasson, R. Semiat, Inhibition of CaCO₃ scaling on RO membranes by trace amounts of zinc ions, *Desalination* 183 (2005) 289–300.
- [22] A. Kai, T. Miki, *Jpn. J. Appl. Phys.* 39 (2000) 1071.
- [33] R. Ketrane B. Saidani, Gil, L. Leleyter, F. Baraud. Efficiency of five scale inhibitors on calcium carbonate precipitation from hard water: Effect of temperature and concentration. *Desalination* 249 (2009) 1397–1404.
- [34] I. Drela, P. Falewicz, S. Kuczkowska, New rapid test for evaluation of scale inhibitors, *Water Res.* 32 (10) (1998) 3188–3191.
- [35] M.M. Reddy, A.R. Hoch, Calcite crystal growth rate inhibition by polycarboxylic acids, *J. Colloid Interface Sci.* 235 (2001) 365–370
- [36] P.V. Brady, W.A. House (Eds.), *Physics and Chemistry of Mineral Surfaces*, CRC Press, New York, 1996, p. 225.

-
- [37] C. Gabrielli, G. Maurin, G. Poindessous, R. Rosset, Nucleation and growth of calciumcarbonate by an electrochemical scaling process, *J. Cryst. Growth* 200 (1999) 236–250
- [25] W. B. White, In *Infrared Spectra of Minerals* ; Mineralogical Society: London, 1974; pp 227-284.
- [26] N. V. Vagenas, A. Gatsouli and C. G. Kontoyannis, *Talanta*, 2003,59, 831–836
- [27] F. A. Andersen and L. J. Brecevic, *Acta Chem. Scand.*, 1991,45, 1018–1024.
- [28] M. Dinamani, P. Vishnu Kamath, R. Seshadri, Electrochemical synthesis of calcium carbonate coatings on stainless steel substrates, *Mater. Res. Bull* 37 (2002) 661–669.